

(19) Japan Patent Office

(11) Publication of Patent Application 49-34573

(51) Int. Cl. (52) Japan Classification

C 23 c 13/02 12 A 25

C 22 c 1/00 13 (7) D 61

10 A 32

Patent Gazette

(44) Publication Date September 14, 1974

Number of Inventions: 1

(18 pages in original Japanese document)

(54) Method of Producing Single Group or Compound Group Material Using Vacuum Vapor Deposition Method

(21) Application Number 45-97169

(22) Filing Date: November 6, 1970

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Brief Explanation of Figures

Figure 1 (a) is a diagram explaining the principle behind one conventional method used to obtain a ternary group material. Figure 1 (b) is a line drawing showing the concentration distribution of the ternary group material obtained here. Figure 2 (a) is a diagram explaining the principle behind one conventional method used to obtain a binary group material. Figure 2 (b) is a line drawing of the concentration distribution of the material obtained here. Figure 3 (a) is a diagram explaining the principle behind a conventional method used to obtain a binary group material. Figure 3 (b) is a line drawing showing the concentration distribution of the material obtained here. Figure 4 (a) is a diagram explaining the principle behind a conventional method used to obtain a ternary group material. Figure 4 (b) is a line drawing of the film thickness distribution of the deposited film obtained here. Next, Figure 5 (a) is a diagram explaining the principle when a single group material is obtained by the method of the present invention. Figure 5 (b) is a line drawing showing the film thickness distribution of the deposited film obtained here. Figure 6 is a diagram explaining the principle behind the principle when a mask having a wedge-shaped opening part is used. Figure 7 (a), (b), (c), Figure 8 (a),(b) and Figure 9 (a),(b) are all diagrams showing another example of the mask opening part shape in all of these. Figure 10 and Figure 11 are respectively diagrams showing another example of the shape of the deposition substrate. Figure 12 and Figure 13 are diagrams explaining the principle behind a combination of a plurality of vaporizing sources and a plurality of opening parts. Furthermore, Figure 14 (a) and Figure 15 (a) are both diagrams explaining the principle behind obtaining a binary group material using the method in the present invention. Figure 14 (b) and Figure 15 (b) are both line drawings showing the concentration distribution of the deposited film obtained using each of the methods above. Figure 16, Figure 17, Figure 18 and Figure 19 are all explanatory diagrams of another layout configuration when a binary group material is obtained using the present invention. Further, Figure 20 (a) is a diagram explaining the principle used to obtain a ternary group material using the method in the present invention. Figure 20 (b) is a line drawing showing the concentration distribution of the deposited film obtained here. Figure 21 is likewise an explanatory diagram of another layout configuration when obtaining a ternary group material. Figure 22 is a diagram showing another example of the shape of the mask opening part. Figure 23 is a diagram showing yet another layout configuration when obtaining a ternary group material. Figure 24 is an explanatory diagram of the layout relation of the opening part and the vaporizing source relative to the substrate when obtaining a ternary group material. Further, Figure 25 (a) is a line drawing showing the concentration distribution of the Pn-In group deposited film obtained in

Practical Embodiment 1 of the present invention. Figure 25 (b) is a line drawing showing the distribution of the lattice constant thereof. Figure 25 (c) is a line drawing showing the changes in the superconductive critical temperature thereof. Figure 26 is a line drawing showing the concentration distribution and the distribution of the superconductive critical temperature of the Pb-In-Sn group deposited film obtained in Practical Embodiment 2 of the present invention.

Detailed Description of Invention

The present invention relates to a method for manufacturing a single- or compound group material using the vacuum vapor deposition method; it relates particularly to a method used to obtain a material such that the film thickness of the material in each of the individual constituents or the composition ratio changes in a linear fashion in accordance with the position on the vapor deposition substrate as a single vapor deposited film.

For example, when a new alloy material is being developed in the field of metallurgy, the composition ratio of the material of each of the constituents is changed over a wide range and tests must be carried out to see at what range of the composition ratio the optimum characteristics can be obtained. Incidentally, separate samples are manufactured such that the composition ratio of the material of each of the constituents is different. This requires far too much time and effort in operations used to make the samples and this is one of the reasons it is difficult to develop new materials.

Recently, a method has been proposed for obtaining a deposited film such that the composition ratio of each of the constituent materials changes over a wide range in keeping with the deposition position by changing the amount of each constituent material deposited in keeping with the position on the substrate when depositing a plurality of constituent elements simultaneously on a single substrate such that a material consisting of a plurality of constituents is deposited using the vacuum vapor deposition method and then using this as a sample.

One of these methods can be seen in the report written by Kennedy et al. (United States) (Journal of Applied Physics, Vol. 36, No. 12, 1965, p. 3808). As shown in Figure 1 (a), three types of vapor deposition sources A, B and C are placed respectively directly beneath vertices a, b and c on triangular vapor deposition substrate P; it makes use of the fact that the distance and the angle of incline from each of the vapor deposition sources changes in accordance with the position on substrate P; and is used to

obtain a deposited film such that the composition ratio (hereinafter simply "concentration") of the materials of each of the constituents changes (that is, there is a distribution of the concentration) depending on the location. However, the concentration distribution of the materials in each of the constituents obtained using this method is characteristic in that the linearity of the distribution deteriorates conspicuously compared to the ternary group phase diagram normally used, an example of which is shown in Figure 1 (b). This means that the position on the substrate and the concentration of the material in each of the constituents are not linearly proportionate so that the method is disadvantageous in that it is difficult to coordinate the position of the deposited film obtained with the composition of the materials.

A second method can be seen in Publication of Examined Patent Application S43-27926. In this method, a plurality of types of band-like vaporizing sources are arrayed so that they radiate virtually in parallel, the deposition substrate is placed so that it is virtually perpendicular to the vaporizing sources; a shielding plate having an edge effect is placed on the end surface so that a semi-shading is delineated between the above-mentioned vaporizing sources and the substrate; the semi-shadings of each of the vaporizing sources are placed so that overlap facing one another on the substrate, each of the vaporizing sources are used for vaporizing simultaneously so that a deposited film consisting of compound group materials having a constituent concentration which changes linearly in the lengthwise direction of each of the vaporizing sources is obtained on the substrate.

For example, when a binary group is used, linear vaporizing sources A and B are arrayed on the left and right of a straight line, as shown in Figure 2 (a), shielding plates Qa, Qb having linear end surfaces a and b extending perpendicular (perpendicular to the level space) to A and B are placed between this and substrate P; a semi-shading of vaporizing source A by end surface a and a semi-shading of vaporizing source B by end surface b overlap on the substrate so that they are opposite one another, the separate materials are deposited simultaneously from vaporizing sources A,B and are deposited on substrate P. Nevertheless, when this takes place, a deposited film consisting of a binary group material having a linear concentration distribution is obtained on substrate P, as shown in Figure 2 (b).

Furthermore, as shown in Figure 3 (a), a deposited film consisting of a binary group material having the linear distribution shown in Figure 3 (b) is obtained by ensuring that the semi-shadings of

vaporizing sources A,B overlap on substrate P using shielding plate Q having end surfaces a',b' which are perpendicular to the vaporizing sources on the left and right end surfaces even when the outer periphery of the shielding plate Q is used as a passage for the substance deposited.

Furthermore, as shown in Figure 4 (a), when a ternary group material is used, three types of vaporizing sources A, B, C centered on a single point u on the deposited surface R are arranged in a radiating pattern so that they are displaced from one another at 120°; a shielding plate Q having the shape of an equilateral triangle is placed on top of this, a deposition substrate P having the shape of an equilateral triangle is placed so that it faces shielding plate Q on top of this; the semi-shadings of vaporizing sources A, B, C which are delineated respectively using the three sides b'c', c'a', a'b' of shielding plate Q overlap one another on substrate P. Therefore, at this time, a deposited film having the three-dimensional phase diagram type concentration distribution shown in Figure 4 (b) is obtained on substrate P.

Thus, in the method disclosed in Publication of Examined Patent Application S43-27926, a deposited film consisting of compound group materials having a linear concentration slope in the lengthwise direction of each of the vaporizing sources can be obtained as long as the distance between the vaporizing source and the substrate is sufficiently larger than the dimensions of the substrate. Nevertheless, in this method, a concentration slope is provided in the lengthwise direction of each of the vaporizing sources using the semi-shading of the vaporizing source formed on the substrate by the end surface of the shielding plate. As a result, the length of each of the vaporizing sources and the position of both ends of these must be determined precisely in order to obtain a deposited film having the desired dimensions and concentration distribution and the crux of the matter here is the manufacturing precision of the vaporizing source.

Taking note of these points, it is an object of the present invention to provide a novel and unique method which makes it possible to obtain a deposited film consisting of a single group or compound group material such that the thickness of the deposited film or the concentration of the constituents changes linearly perpendicular to each of the above-mentioned deposition sources using Å^{-1} units or a plurality of linear vaporizing sources of any length without using the semi-shading effect indicated above.

This means that the present invention is characteristic in that a mask provided with one or a

plurality of triangular (or wedge-shaped) opening parts the opening width of which when measured in a direction parallel to each of the corresponding vaporizing sources changes linearly between one or a plurality of linear vaporizing sources and a single deposition substrate; the substance to be deposited is deposited on the above-mentioned substrate passing through each of the corresponding opening parts from each of the above-mentioned vaporizing sources so that a deposited film consisting of a single group or compound group material is formed such that the thickness of the deposited film or the concentration of the constituents changes linearly perpendicular to each of the above-mentioned vaporizing sources on the above-mentioned substrate.

Therefore the basic principle at work in the present invention lies in the fact that when we observe each of the vaporizing sources through each of the corresponding triangular (or wedge-shaped) opening parts from the top of the substrate, using the fact that as we shift our angle of vision on the top of the substrate to a direction which is at a right angle to each of the above-mentioned vaporizing sources, the length of the depositing source which can be seen from that changes linearly and a deposited film can be obtained such that the amount of deposition (film thickness or film concentration) of the materials from each of the vaporizing sources changes linearly.

Next, we shall explain a mode of working the present invention referring to the figures.

First, we shall explain how to obtain a deposited film consisting of a single group material having a film thickness which changes linearly using the method in the present invention.

Figure 5 (a) shows the layout configuration which embodies the principle of the deposition device used to obtain the deposited film made of the single group material using the present invention. In the same figure, A shows the vaporizing source; Q shows the mask; and P shows the substrate for deposition. Substrate P and mask Q are placed respectively at intervals h_1 and h_2 parallel to plane surface R (hereinafter "deposited surface") comprising vaporizing source A and these are accommodated inside the same vacuum chamber (not shown in the figure). Vaporizing source A is linear and has a narrow width extending at a right angle to straight line l; and the amount deposited is the same regardless of the location. Then a triangular opening part Ma having a bottom side b'c' (length l_2) which is parallel to vertex a' and vaporizing source A is placed on mask Q. As a result, the width of the opening part measured in a direction parallel to vaporizing source A changes linearly from 0 to l_2 perpendicular (direction of straight line m) to vaporizing source A. Furthermore, the length of opening

part Ma is measured perpendicular to vaporizing source A is b_2 .

In addition, the length in the direction (direction of straight line n) perpendicular to the vaporizing source A is d_1 and the width parallel to this is l_1 and the relation $d_2/d_1 = h_2/h_1$ results. Then, vaporizing source A and bottom side b'c' of opening part Ma and right end p_1 of substrate P are on the same plane surface. Furthermore, vertex a of vaporizing source A and opening part Ma and left end p_3 of substrate P are on the same plane surface. Moreover, the distance h_1 between substrate P and vaporizing source A is large enough (several times or more) for dimensions d_1, l_1 of substrate P.

When the desired material is deposited from vaporizing source A in this state, a deposited film is obtained on substrate P such that the film thickness changes in the direction perpendicular to vaporizing source A such that there is no change in the film thickness in a direction which is parallel to vaporizing source A, as shown in Figure 5 (b). Therefore, when three vantage points p_1, p_2, p_3 in the direction perpendicular to vaporizing source A on substrate P are considered, the effective width of the opening part when vaporizing source A is seen from point p_1 is l_2 ; when seen from intermediate point p_2 , it is $l_2/2$; and when seen from point p_3 , it is 0. As a result, the part of the length which is $L = h_1/(h_1 - h_2) \times l_2$ of vaporizing source A is seen from point p_1 ; and no part of vaporizing source A can be seen from point p_3 . Thus, the film thickness at any point on substrate P is proportionate to the length of vaporizing source A which can be seen through opening part Ma from that point so that when the film thickness at point p_1 is 100, the film thickness at point p_2 is 50 and the film thickness at point p_3 is 0. Thus, the thickness of the deposited film changes linearly in the direction perpendicular to vaporizing source A.

Next, considering a straight line parallel to vaporizing source A passing through point p_1 on substrate P, the effective width of the opening is always l_2 even when vaporizing source A is viewed from any point on the straight line. As a result, the length of the vaporizing source which can be seen from this line is always L and only the center line thereof moves in the lengthwise direction of the vaporizing source corresponding to the position of the visual point on the substrate. Furthermore, when the straight line parallel to vaporizing source A is considered through point p_2 , the effective width of the opening is always $l_2/2$ even when the visual point is moved to any point on this straight line and the length of the vaporizing source that can be seen from above this line is always $L/2$. Likewise, it is completely impossible to view the vaporizing source from any point on a straight line which is parallel to vaporizing source A through point p_3 . As a result, there is no change whatsoever in the thickness of

the deposited film in the direction parallel to vaporizing source A.

As is obvious from the above-mentioned explanation, the present invention can be used to obtain a deposited film which has linear changes in the thickness of the film in the direction perpendicular to the vaporizing source on the substrate and which does not have linear changes in the thickness of the film in a direction parallel to the vaporizing source using a single linear vaporizing source and a single triangular opening part. Thus, in the method in the present invention, changes in the film thickness of the film deposited are not made using a semi-shading parts as was the case in the conventional technique so that there were options as to the length of the vaporizing source so that there was a large degree of freedom in producing it. This means as long as the length of the vaporizing source is made larger than value $l_3 = h_1 l_2 + h_2 l_1 / h_1 - h_2$ to which was added field of vision center displacement $dL = h_2 / (h_1 - h_2) \times l_1$ corresponding to width l_1 of substrate P on length $L = h_1 / (h_1 - h_2) \times l_2$ which can be viewed at point p_1 indicated above, any length is suitable.

Furthermore, the distance h_1 of the substrate should be selected so that it is several times or more than substrate dimensions d_1, l_1 in order to make the displacement from the linearity of the distribution of the thickness of the substrate--occurring when the distance up to the vaporizing substrate and the angle of incline are different due to the position on the substrate--small enough so that it can be ignored.

As an example of this, in the layout confirmation in Figure 5 (a), when $h_1 = 30$ cm, $h_2 = 10$ cm, $d_1 = 9$ cm, $l_1 = 2$ cm and $l_2 = 2$ cm in the configuration of the placement shown in Figure 5 (a), we get $d_2 = 3$ cm, $L = 3$ cm and $l_3 = 4$ cm. Based on this type of setting, an indium thin film having the linear film thickness distribution shown in Figure 5 (b) can be obtained as desired by actually depositing the indium on substrate P using a board-shaped heater measuring 5 cm long and 3 mm wide as vaporizing source A. In general, a film thickness distribution with good reproducibility can be obtained using a high vacuum exhaust group, increasing the deposition efficiency of the substance to be deposited by heating or cooling the substrate and reducing the movement on the surface.

Furthermore, in the above-mentioned explanation, we presented an example in which a triangular form was used for the opening part of the mask. However, a wedge-shaped one having a bottom side $b'c'$ may be used as the opening part Ma , as shown in Figure 6. What is important here is that it have a part Ma such that the opening width changes linearly when measured in a direction parallel to vaporizing source A over the range indicated by $d_2 = h_2 / h_1 \times d_1$ in a direction perpendicular to vaporizing source A

from vertex a' in the center of this wedge-shaped opening. This means that considering the length of vaporizing source A from a position removed from substrate P having prescribed dimensions is unrelated to the film thickness distribution on substrate P. As a result, as long as length d_2 is secured, an opening part which exceeds this is optional. Based on this, it can be seen that even if there is an opening part which exceeds d_2 , that part may have any shape. Figure 7 (a) shows an example of extending the opening part Ma having prescribed dimensions to the right at the vertex as is. Figure 7 (b) shows an example of opening part Ma having prescribed dimensions wherein half of the opening part is lozenge shaped. Figure 7 (c) shows an example of extending the right end of opening part Ma having prescribed dimensions so that it is rectangular.

Furthermore, opening part Ma by no means need extend along straight line m which is drawn so that it is perpendicular to vaporizing source A passing through vertex a . As shown in Figure 8 (a) and Figure 8 (b) it may extend in a direction at an incline to straight line m . However, it should be noted that here, substrate P should either be inclined in the same direction or the length of the vaporizing source should be sufficiently large.

Moreover, in an extreme case, opening part Ma should be bent so that it is discontinuous in the middle, as shown in Figure 9 (a) and it may curve to form a curved line, as shown in Figure 9 (b). What is important is that the width of the opening extending along length d_2 change so that it is sufficiently linear.

Thus, when the length of vaporizing source A is sufficiently long, the shape of the opening part can be selected with a considerable degree of freedom. In the explanation provided below, we will mainly describe use of a triangular opening part. However, needless to say, the present invention comprises the above-mentioned variant.

We also provided an example using a rectangle for substrate P in the above-mentioned explanation. However, there is a considerable degree of freedom in selecting the shape of this substrate P in accordance with the shape of the opening part. Figure 10 shows an example using a triangular substrate. Figure 11 shows an example in which the direction of substrate P is inclined from n to n' as the center line of opening part Ma is inclined from m to m' also using a triangular substrate.

Moreover, in the above-mentioned explanation, we used an example in which we used a single

vaporizing source and a single opening part. However, a plurality of vaporizing sources used to vaporize the same material and a plurality of opening parts corresponding to these may also be used. Figure 12 and Figure 13 show examples of deposition on a single substrate P using a mask having two vaporizing sources A,A' and two opening parts Ma, Ma'. As a result, the former is an example of placing vaporizing sources A,A' in parallel and the latter is an example of placing them on a single straight line.

Next, we shall describe the method of obtaining a deposited film consisting of a binary group material such that the concentration of the constituents changes linearly by applying the above-mentioned principle.

Figure 14 (a) shows the layout configuration which is the principle of the deposition device is when used to obtain a deposited film of the binary group materials using the method in the present invention. In the same figure A, B are vaporizing sources used to vaporize different types of materials; Ma, Mb are opening parts corresponding respectively to vaporizing sources A,B; and P is a vaporizing substrate. Thus, opening parts Ma and Mb are placed so that they are opposite one another (back to back) centered on straight line m. Here, when the distance between vaporizing sources A, B is r_1 and the interval between opening parts Ma, Mb is r_2 , we set the dimensions of each of the parts so that the relation $(h_1 - h_2)/h_1 = (d_2 + r_2)/r_1$ is satisfied, exclusive of the conditions $d_1/d_2 = h_2/h_1$ indicated above. In an example of this, if $h_1 = 30$ cm, $h_2 = 10$ cm, $d_1 = 9$ cm, $l_1 = 2$ cm, $l_2 = 2$ cm and $r_1 = 9$ cm, we get $d_2 = 3$ cm, $l_3 = 4$ cm and $r_2 = 3$ cm.

When two different materials are vaporized simultaneously from vaporizing sources A, B under these conditions, the two types of materials overlap on substrate P and are deposited and a deposited film having the concentration distribution shown in Figure 14 (b) is obtained. This means that the amount of material (constituent A) deposited from vaporizing source A changes linearly from 0 to 100 from point p1 towards point p2. The amount of material (constituent B) deposited from vaporizing source B also changes linearly from 0 to 100 and conversely from point p1 towards point p2. Thus, when the entire amount of both of the above-mentioned constituents deposited is made equal in weight, the concentration distribution obtained changes linearly in weight percent. Furthermore, when the entire amount of both constituents deposited is made equal in atomic number or in number of molecules, the concentration distribution obtained changes linearly as a molecular percentage. This can be regulated freely by controlling the vaporizing speed of vaporizing sources A,B.

Thus, when the method in the present invention is used, a deposited film consisting of binary group materials can be obtained such that the concentration distribution changes linearly perpendicular to both deposition sources on a single substrate P by combining two types of vaporizing sources and a mask having two opening parts opposite this.

Furthermore, as shown in Figure 15 (a), even when opening parts Ma, Mb are placed so that their vertices face one another, a deposited film consisting of a binary group material having a linear concentration distribution perpendicular to both vaporizing sources can be obtained, as shown in Figure 15 (b).

Furthermore, $r_2 = 0$ by bringing the vaporizing source close and opening parts Ma and Mb may be joined together and made into a single lozenge-shaped opening, as shown in Figure 16. The vertices of opening parts Ma and Mb may be made to coincide by changing the ratio of h_1 and h_2 , as shown in Figure 17. Moreover, it can be seen from Figure 17 that opening part Ma is equivalent to Ma' and that opening part Mb is equivalent to Mb'. Based on this, it can be seen that any combination of opening parts is possible such as: Ma and Mb; Ma and Mb'; Ma' and Mb; and Ma' and Mb'.

In addition, vaporizing sources A,B may be placed in a straight line and opening parts Ma, Mb may be placed so that they face one another and set so that they are parallel to the vaporizing source, as shown in Figure 18. Moreover, opening parts Ma and Mb may be placed so that the back sides of these are facing, both of these may be extended inside so that they exceed a prescribed length d_2 and a single lozenge-shaped opening may be used for the entire body, as shown in Figure 19.

Next, we shall describe how to obtain a deposited film consisting of a ternary group material whose constituent concentration changes linearly using the method in the present invention.

Figure 20 (a) shows an example of forming a deposited film consisting of ternary group materials on a single substrate P using a combination of three types of vaporizing sources A, B, C and a mask Q having a single opening Mo. Here, vaporizing sources A, B, C are placed so that they make up a triangle having sides $\alpha\beta\gamma$. Opening Mo makes up a triangle $a'b'c'$ which is similar to the above-mentioned triangle $\alpha\beta\gamma$. Furthermore, substrate P is shaped like a triangle abc which is similar to the above-mentioned triangle $a'b'c'$. Then the similarity ratio of triangle abc and triangle $a'b'c'$ is h_1/h_2 and the similarity ratio of triangle $\alpha\beta\gamma$ and $a'b'c'$ is $h_1/(h_1 - h_2)$. An example of this is as follows: when the

length of one side is $h_1 = 30$ cm $h_2 = 15$ cm using a 10 cm substrate shaped like an equilateral triangle, opening Mo is shaped like an equilateral triangle one side of which is 5 cm long and the prescribed length of each of the deposition sources is 10 cm.

When three types of materials are vaporized simultaneously from vaporizing sources A, B, C, under these conditions, the ternary group material having the concentration distribution shown in Figure 20 (b) is deposited on substrate P. This means that triangular opening Mo functions as an opening Ma having bottom side $b'c'$ and vertex a' and the concentration of constituent A on substrate P is changed linearly. Likewise, opening Mo functions as opening parts Mb, Mc having vertices b',c' respectively relative to vaporizing sources B,C and the concentration of constituent B, C on substrate P is changed linearly in both directions *be* and *of*.

Furthermore, the deposition process need not involve vaporizing three types of materials simultaneously and needless to say vaporizing may be carried out sequentially or alternately. Moreover, it can be easily understood from the explanation given for the single group material that the shape of substrate P is not restricted to an equilateral triangle. This is advantageous when the concentration slope for the specific constituent materials is mild and when studying the difference in the properties of the materials brought on by slight changes in the concentration.

Moreover, in the explanation given previously, 5 types of vaporizing sources A,B,C were selected which had the same length on each side of triangle $\alpha\beta\gamma$ so that the sides of two types of vaporizing sources made contact with one another at the position of each vertex. This was inappropriate as it made it difficult to produce the vaporizing source. In order to avoid this, the operation shown in Figure 21 should be carried out. Therefore, Figure 21 shows moving vaporizing sources A,B,C--placed so that they make contact with the end part on the original triangle $\alpha\beta\gamma$ to the middle part of each side of triangle $\alpha'\beta'\gamma'$ K times ($K \geq 1$) at the same original length; so that the opening which was originally Mo expands $(K+1)/2$. This means that by moving vaporizing sources A,B,C on top of triangle $\alpha'\beta'\gamma'$, the prescribed dimensions of the opening part corresponding to each of the vaporizing sources are no different from the dimensions of the original opening part Mo. However, each of the vertices are shifted respectively to a'', b'', c'' thereby becoming an overall expanded opening Mo'. For example, the part of triangle $a''b''c''$ on opening Mo' (this has the same dimensions as Mo) becomes opening part Ma relative to vaporizing source A. When this is carried out, the three types of vaporizing sources no longer make

contact with one another inside the parameters of prescribed length L. As a result, the prescribed length of each vaporizing source can be secured sufficiently and it can be manufactured easily.

In addition, when $K = 3$ in the example above, the dimensions of opening Mo' become twice the prescribed dimensions of opening Mo when $K = 1$. As a result, when $K > 3$, a mask having separate opening parts Ma , Mb , Mc can be used respectively for each of vaporizing sources A, B, C, as shown in Figure 22.

Furthermore, as shown in Figure 23, vaporizing sources A, B, C arranged on the original triangle $\alpha\beta\gamma$ may be moved on backward facing triangle $\alpha''\beta''\gamma''$ on the original length so that three corresponding openings Ma , Mb , Mc may be placed respectively on each of vaporizing sources A, B, C instead of the original single opening Mo . In addition, even in this case, each of the vaporizing sources should be moved somewhat outside of each side of triangle $\alpha''\beta''\gamma''$ so that the three deposition sources do not make contact with one another. At that time, openings Ma , Mb , Mc of the mask should be moved correspondingly outside.

Based on these observations we can understand the following. Namely, as shown in Fig. 24, when a combination of three types of vaporizing source materials A_1, B_1, C_1 and a single opening M_1 deposit three types of materials on a single substrate P, (namely, refer to Fig. 20) when the opening is moved to M_4 , the vaporizing source moves to A_4, B_4, C_4 and when these are moved to M_5 , they move to A_5, B_5, C_5 . As a result, if A_1, B_1 remain as is and only C_1 is moved to C_4 , by using the combination of vaporizing sources A_1, B_1, C_4 , we get two combinations: M_1 corresponding to openings A_1, B_1 ; and M_4 corresponding to C_4 . If we move A_1 to A_5 and make a combination of vaporizing sources A_5, B_4, C_4 from this state, we get a combination of three openings M_5, M_1, M_4 . Then, this combination is equivalent using $K = 3$ in Figure 21. Likewise, when the vaporizing sources are made into a combination of A_4, B_6, C_5 , the combination of openings becomes M_4, M_6, M_5 and this corresponds to what is shown in Figure 23.

Thus, conversely, if the combination of openings is set first to M_1, M_2 , a combination of six openings - $A_1, A_2, B_1, B_2, C_1, C_2$ -may be used as the vaporizing source and three combinations of any one of these materials may be made. Likewise, when the combination of openings consists of three openings-- M_1, M_2, M_4 --a combination of nine openings such as $A_1, A_2, A_4, B_1, B_2, B_4, C_1, C_2, C_4$ may be used as the vaporizing source. A combination of six of these consisting of two each of these materials or a combination of three of any one of these may be used. Thus, by increasing the number of openings the

methods of combining the vaporizing sources increase infinitely.

Moreover, the above-mentioned explanation referred to a combination of the same number of vaporizing sources for three types of materials. However, when differences are made in the amount of each material deposited, a difference can be made in the number of vaporizing sources for each material. For example, in Figure 24, two opening parts, M_1 and M_2 are used; two each such as A_1, A_2, B_1, B_2 are used for constituents A,B as the vaporizing source; either C_1 or C_2 is used for constituent C; and the amount of vaporizing carried out by the vaporizing source for constituent C should be twice that of constituents A,B.

Above, we explained how to make a single-group, binary-group and ternary-group material using the method in the present invention. However, it can readily be understood that the method in the present invention can further be applied to obtain a quaternary-, quinary- or greater group material. For example, when a quaternary group material is to be obtained, the fourth material can be stacked on a ternary group deposited film or deposition may be carried out simultaneously using a combination of four types of vaporizing sources and four wedge-shaped opening parts (or the position at each of the vertices of a square opening part may be used). Furthermore, the composition in the film thickness direction can be made uniform by heat treatment following deposition in a group which can be subjected to diffusion processing.

Then, a wire rod of the desired material itself may be directly heated and vaporized as a linear vaporizing source in the present invention. The desired material may be coated onto the surface of a linear or an L-shaped heater and the material covered by plating and other methods, or a linear heater and the desired material may be twisted together. A narrow port-type heater may also be used. Furthermore, glass and other ceramic, a metal plate and a silicon and sodium chloride cleavage plane may be used as a deposition substrate. Glass and ceramic may also be used in addition to molybdenum and other metal plates.

Next, we shall describe practical embodiments of the present invention.

Practical Embodiment 1

First we shall explain how to obtain a sample having a phase diagram type concentration distribution of a Pb-In binary group.

In the placement configuration shown in Figure 15 (a), $h_1 = 30$ cm, $h_2 = 10$ cm, $d_1 = 9$ cm, $d_2 = 3$ cm, $l_1 = 2$ cm, $l_2 = 2$ cm, $r_1 = 9$ cm and $r_2 = 3$ cm and we used a molybdenum mask on mask Q using a slide glass on substrate P, using a band-shaped port-type heater which was 5 cm long and 3 mm wide as vaporizing sources A,B. We weighed out 99.999 % pure lead lumps and indium lumps so that the atomic weight ratio was 207: 115, inserted them respectively in ports A,B and discharged the air inside a bell jar such that it reached a vacuum of approximately 10^{-6} mmHg. First, we cleaned the surface of the substrate by bombarding it in this state. Then we gradually passed a direct current or an alternating current to the heater resistance of ports A,B. We carried out preliminary heating on the lead lumps or indium lumps inside the port melted and spread evenly onto the board. Then, we closed opening parts Ma, Mb of the mask in advance, opened the shutter, maintained the heater current so that it was nearly uniform and carried out deposition. Next, we estimated that the materials on the port would almost completely be eliminated, cut the heater current and waited for the temperature of the substrate to return to room temperature. Then, we released the vacuum and removed substrate P. Further, we placed this in an electric furnace and carried out diffused heat processing for 2 hours at 150°C in a vacuum of approximately 1×10^{-6} mmHg.

We slit the deposited film obtained in this way at appropriate intervals in the lengthwise direction on the entire substrate. We measured respectively the film thickness distribution for each small fragment using a Sloan ångstrometer; the alloy composition ratio (atom %) using an x-ray microanalyzer; the fixing of the crystalline structure using a device error x-ray analytical method; and superconductor critical temperature T_c using the four-terminal resistivity method. As a result, the concentration distribution of the deposited film exhibited extremely good linearity as shown in Figure 25 (a). Furthermore, the changes in lattice constant and axial ratio of the crystals are shown in Figure 25 (b). Changes in critical temperature T_c are shown in Figure 25 (c). Thus, the concentration distribution of each of the constituents in the deposited film obtained has a linear proportional relationship to the position in the lengthwise direction of the substrate (that is, the direction perpendicular to the vaporizing source).

Practical Embodiment 2

Next, we shall describe how to obtain a sample having the Pb-In-Sn ternary state phase type concentration distribution.

In the placement configuration shown in Figure 21 (a), $b_1 = 30$ cm and $h_2 = 15$ cm. We used a glass plate that was shaped similar to an equilateral triangle with a 10 cm long side as substrate P and used a molybdenum plate having an opening Mo' shaped similar to an equilateral triangle with a 5.5 cm long side as a mask. We also used 11 cm long, 3 mm wide port-type heaters as vaporizing sources A,B,C and placed these in the center of each side 12 cm long of an equilateral triangle $\alpha\beta\gamma$. We weighed out 99.999 % pure In, Pb, Sn respectively so that the weight ratio was equal to the atomic weight ratio (115:207:119) and inserted them in ports A,B,C. From this point onward, we carried out deposition and heat treatment just as we did in the previous practical embodiment.

The concentration distribution of the deposited film obtained as a result of this coincided extremely well with that in the regular ternary state phase as shown in Figure 26. Furthermore, the numbers in Figure 26 shows the results of measuring the superconductive critical temperature in each of the constituent ratios.

As can be understood from the above-mentioned explanation, when the method in the present invention is used, a mask having one or a plurality of openings having an opening width which changes linearly and which is parallel in the lengthwise direction of the vaporizing sources with one or a plurality of linear vaporizing sources so that a single group or a compound group material characterized by linear changes in the direction perpendicular to each of the vaporizing sources on the substrate can be obtained; and which has a principle different to that of the conventional half-shading. As a result, any length is suitable for the vaporizing sources as long as it is at least the prescribed length so that it is easy to produce a vaporizing source.

Furthermore, needless to say, the method in the present invention is used not only in simply producing alloy samples but it can be applied for any combination of all the materials which can be usually deposited.

(57) Claim

1. A method of producing a single group or complex group material characterized as setting in place a mask having one or a plurality of triangular or wedge-shaped opening parts measured in the direction parallel to each corresponding vaporizing source between one or a plurality of linear vaporizing sources and a single deposition substrate, depositing the substance deposited from each of the above-mentioned

vaporizing sources on the above-mentioned substrate through each of the corresponding vaporizing sources mentioned above so that a deposited film can be obtained such that the deposited film thickness or constituent concentration changes in a linear fashion in the direction perpendicular to each of the above-mentioned vaporizing sources.

Figure 1

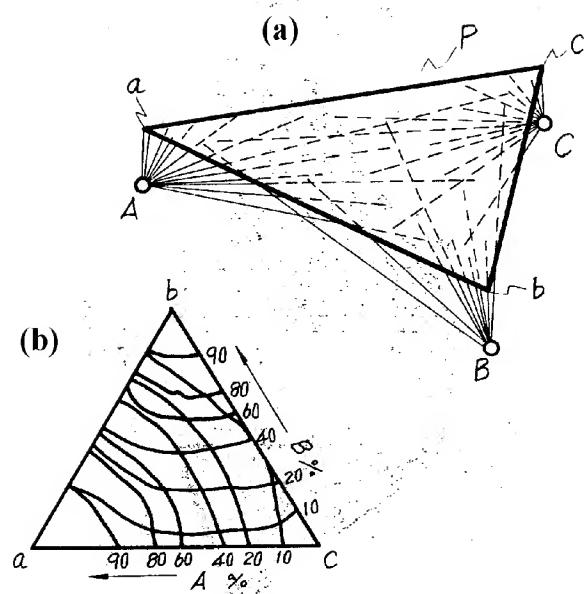


Figure 2

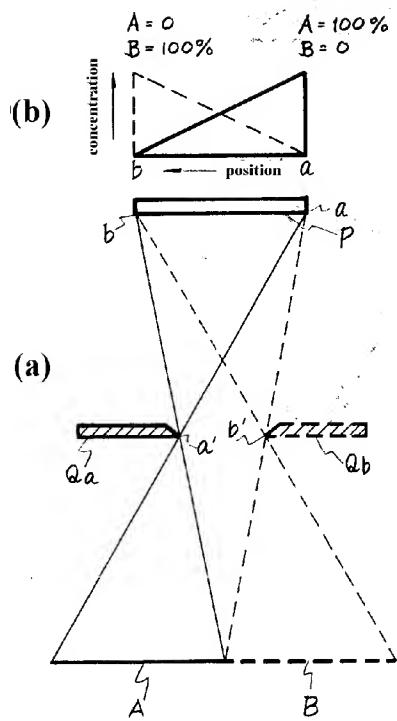


Figure 3

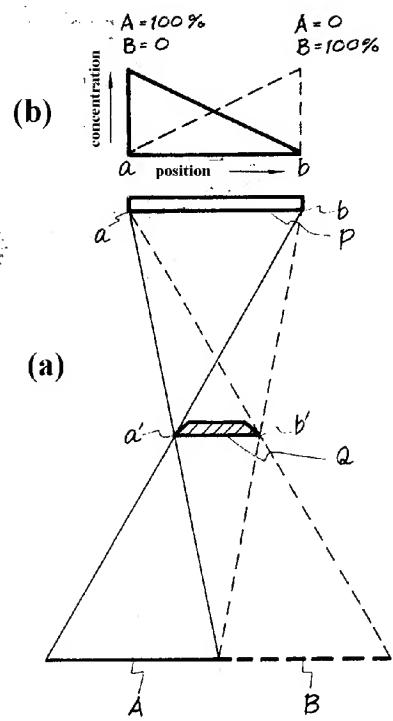
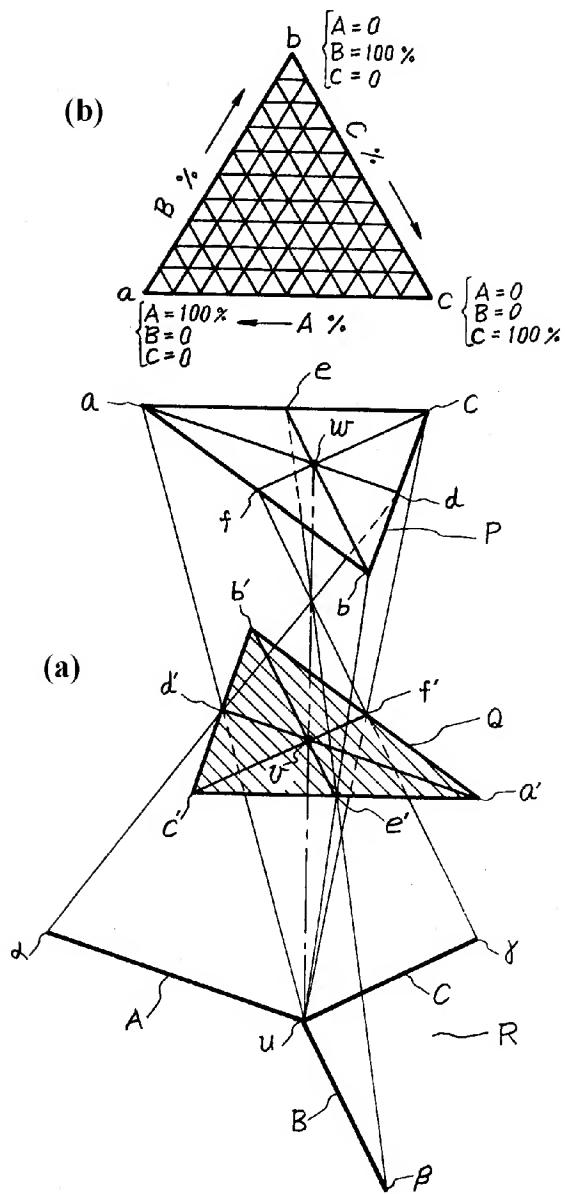


Figure 4



(b)

Figure 5

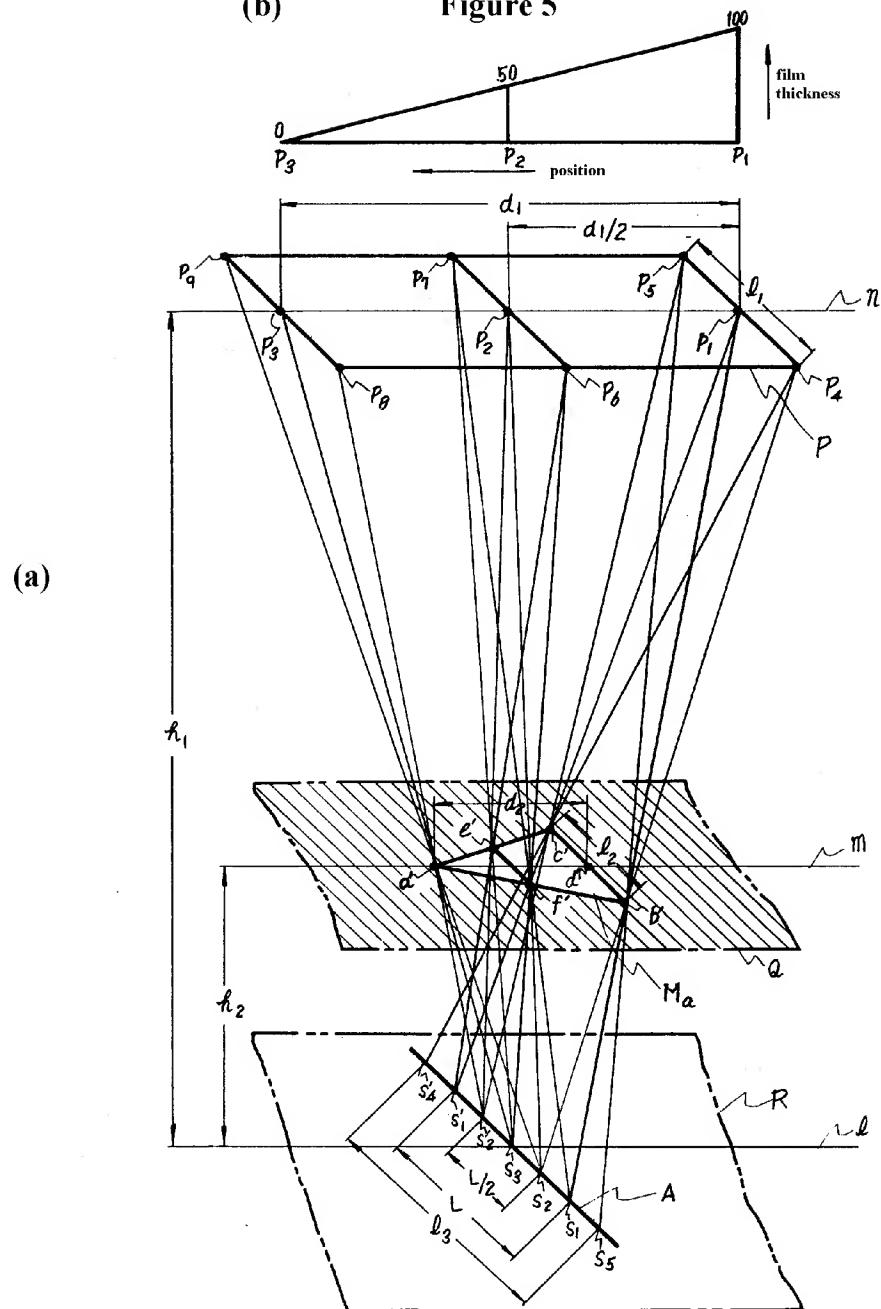


Figure 6

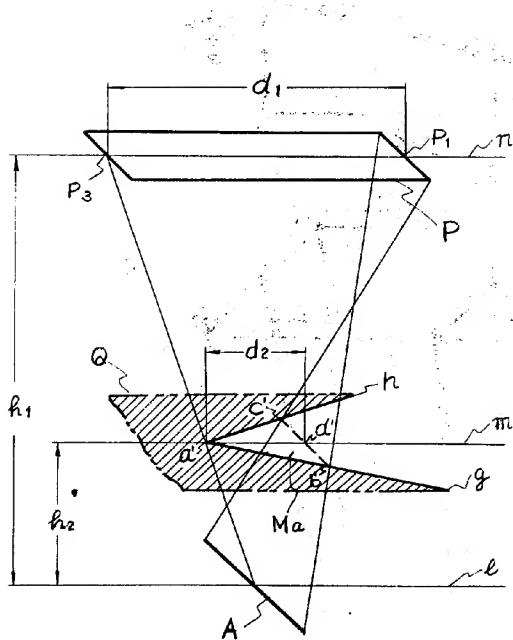


Figure 7

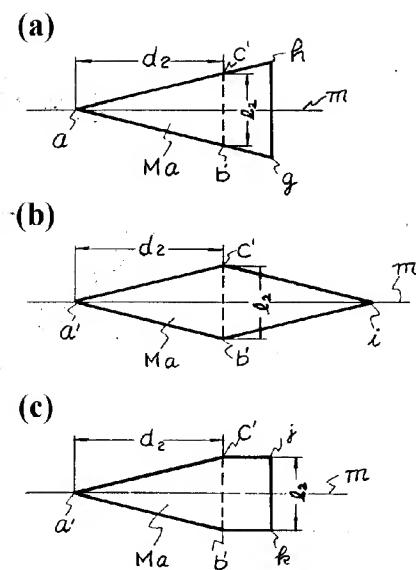


Figure 8

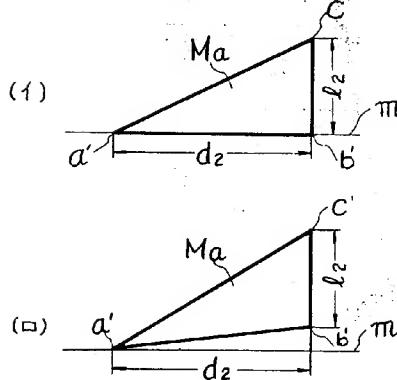


Figure 9

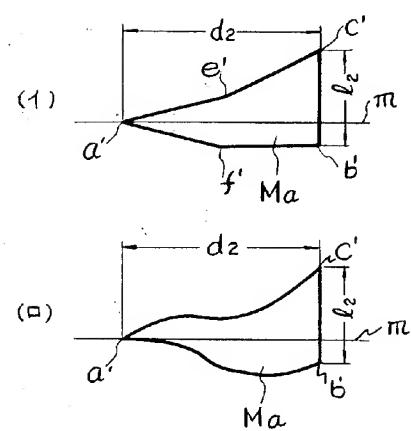


Figure 10

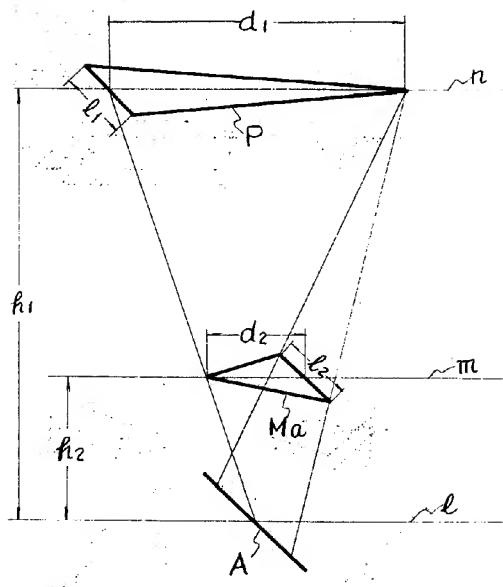


Figure 11

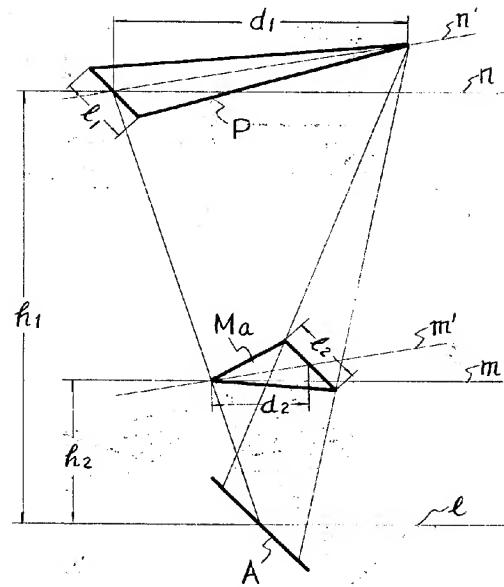


Figure 12

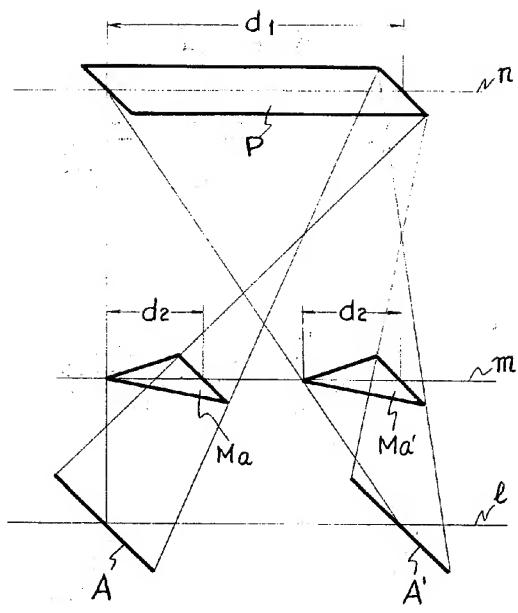


Figure 13

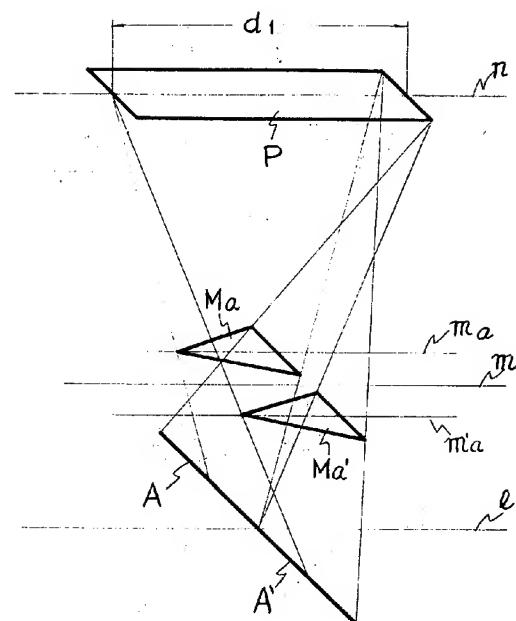


Figure 14

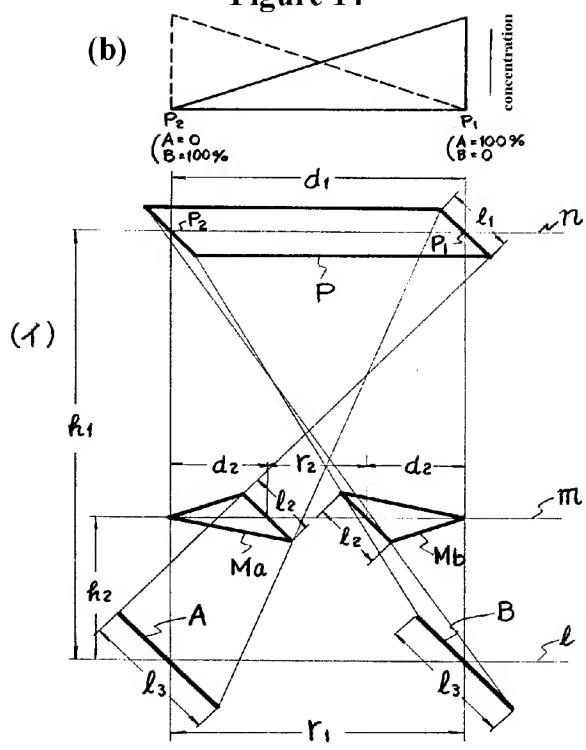


Figure 15

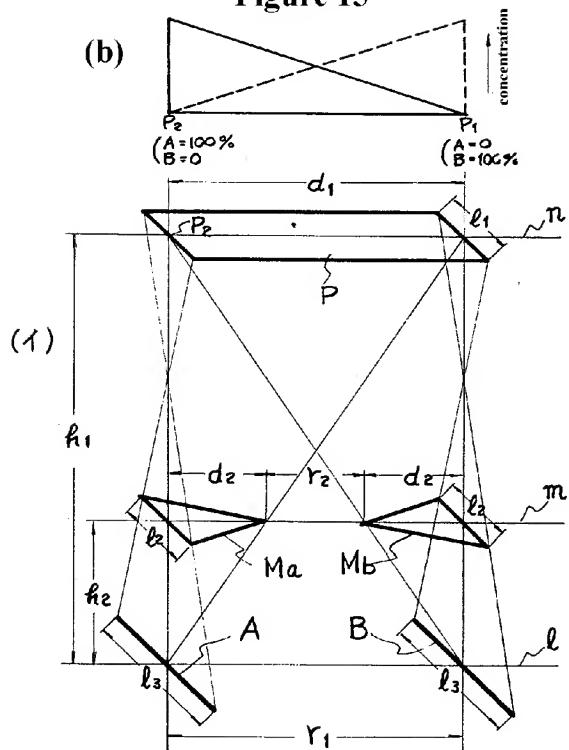


Figure 16

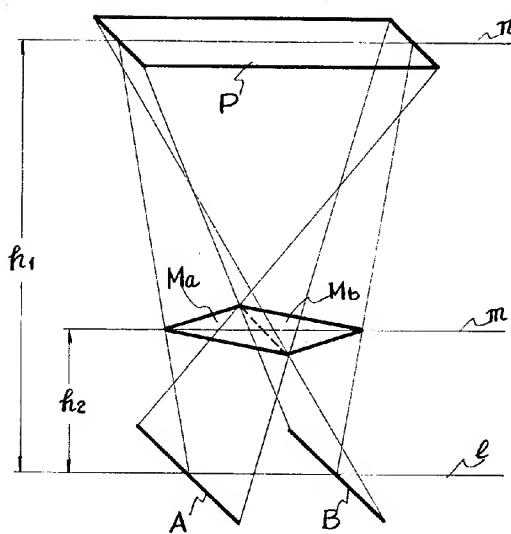


Figure 17

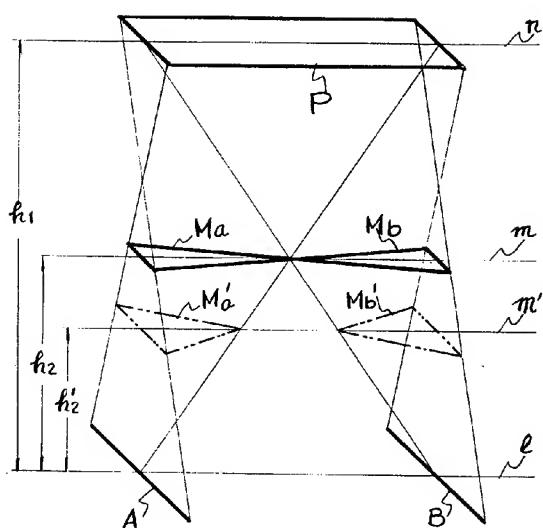


Figure 18

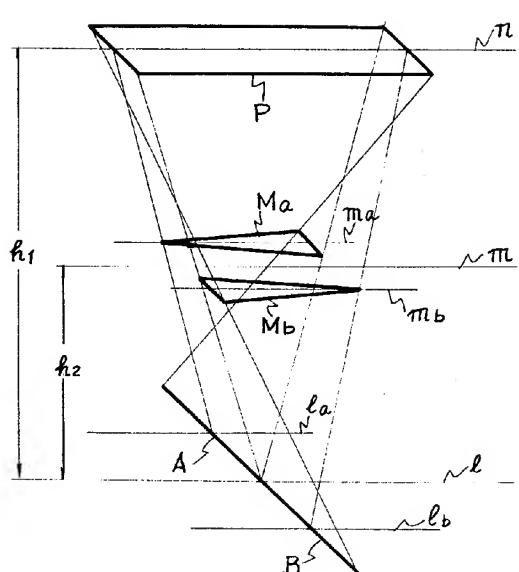
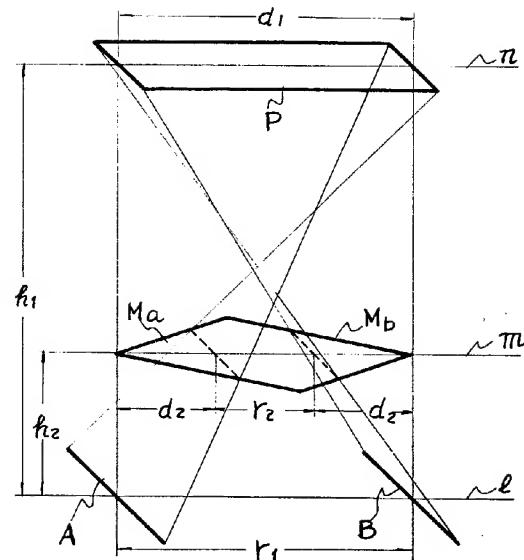
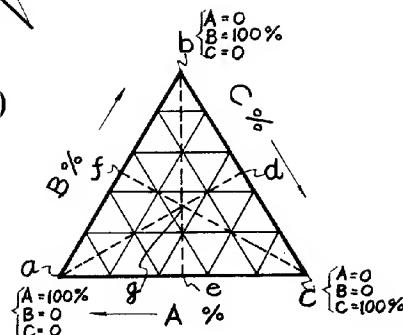


Figure 19



(b)



(a)

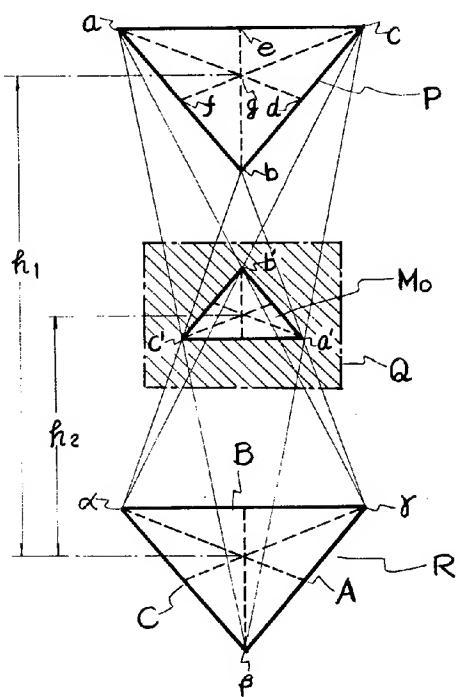


Figure 20

Figure 21

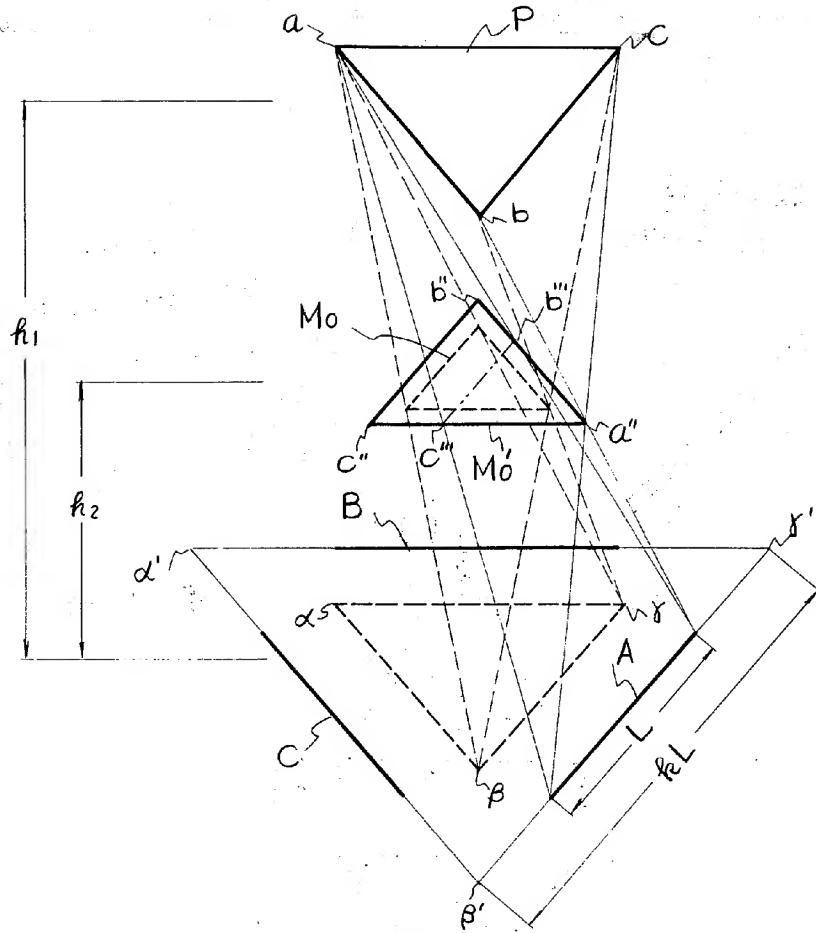


Figure 22

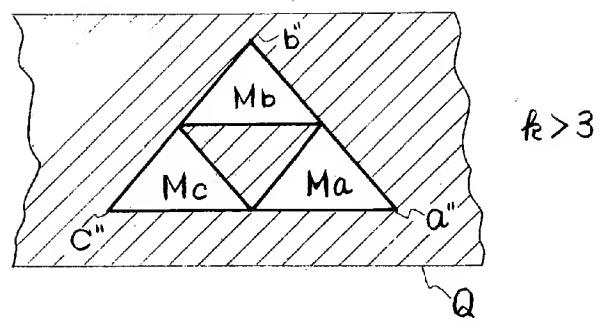


Figure 23

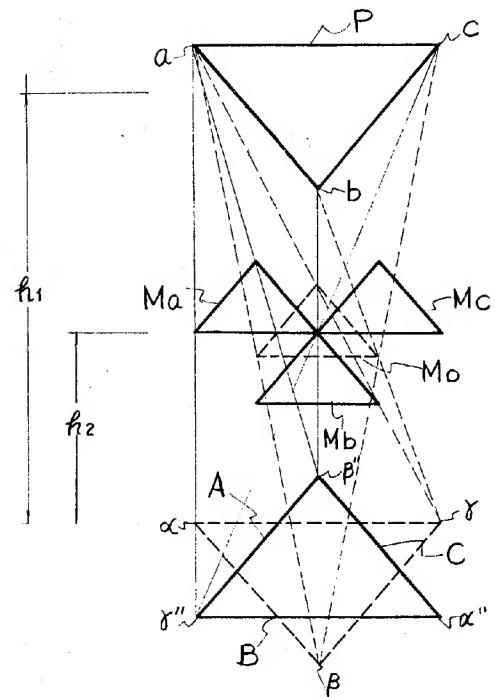


Figure 24

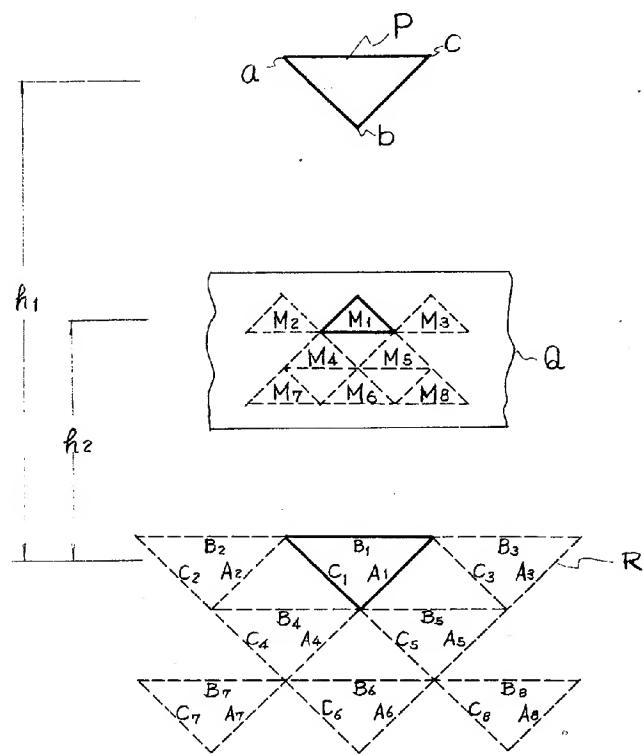


Figure 25

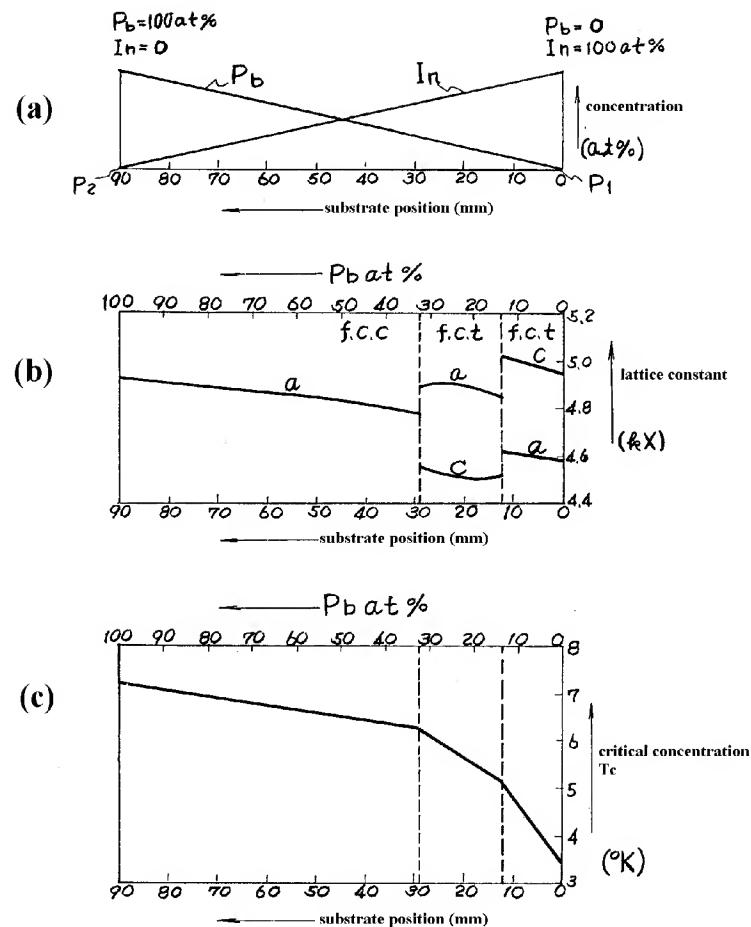
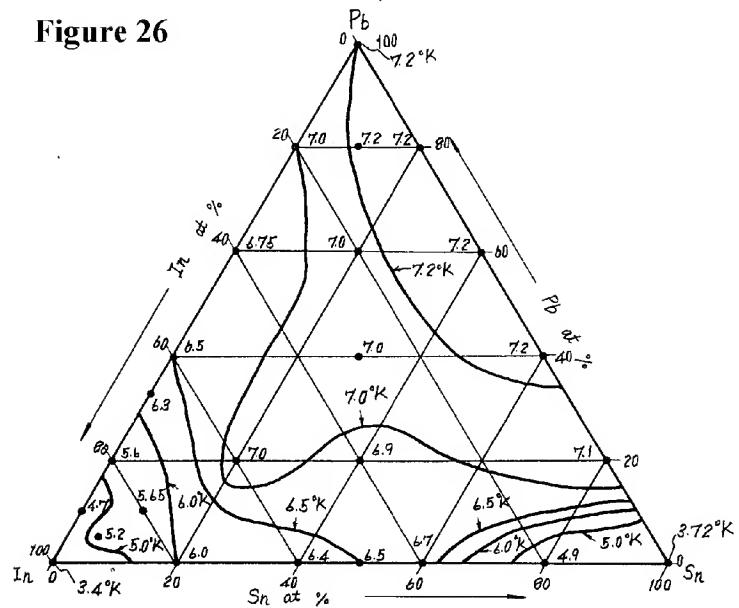


Figure 26



⑤1 Int. Cl. ⑤2 日本分類
C 23 c 13/02 12 A 25
C 22 c 1/00 13(7) D 61
10 A 32

⑯ 日本国特許庁

⑪ 特許出願公告

昭49-34573

特許公報

⑭ 公告 昭和49年(1974)9月14日

発明の数 1

(全18頁)

1

⑯ 真空蒸着法による単元系もしくは複元系材料の
製造方法

⑯ 特 願 昭45-97169

⑯ 出 願 昭45(1970)11月6日

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図面の簡単な説明

第1図イは従来の3元系材料を得るための一方
法の原理説明図、同図ロはそれにおいて得られる
3元系材料の濃度分布を示す線図、第2図イは従
来の2元系材料を得るための一方法の原理説明図、
同図ロはそれにおいて得られる材料の濃度分布を
示す線図、第3図イは従来の2元系材料を得るた
めの他の一方法の原理説明図、同図ロはそれにお
いて得られる材料の濃度分布を示す線図、第4図
イは従来の3元系材料を得るための他の一方法の
原理説明図、同図ロはそれにおいて得られる材料
の濃度分布を示す線図である。つぎに、第5図イ
は本発明の方法により1元系材料を得る場合の原
理説明図、同図ロはそれにおいて得られる蒸着膜
の膜厚分布を示す線図、第6図はくさび状開口部
を有するマスクを用いる場合の原理説明図、第7
図イ、ロ、ハ、第8図イ、ロおよび第9図イ、ロ
はいずれもマスク開口部形状の他の一例を示す図、
第10図および第11図はそれぞれ蒸着基板形状

2

の他の一例を示す図、第12図および第13図は
いずれも複数の蒸発源と複数の開口部を組合せて
用いる場合の原理説明図である。また、第14図
イおよび第15図イはいずれも本発明の方法によ
り2元系材料を得る場合の原理説明図、第14図
ロおよび第15図ロは上記の各場合に得られる蒸
着膜の濃度分布を示す線図、第16図、第17図、
第18図および第19図はいずれも本発明により
2元系材料を得る場合の他の配置構成の説明図で
ある。さらに、第20図イは本発明の方法により
3元系材料を得る場合の原理説明図、同図ロはそ
れにおいて得られる蒸着膜の濃度分布を示す線図、
第21図は同じく3元系材料を得る場合の他の配
置構成の説明図、第22図はマスクの開口部形状
の他の一例を示す図、第23図は3元系材料を得
る場合のさらに他の配置構成を示す図、第24図
は3元系材料を得る場合の基板に対する開口部と
蒸発源の配置関係の説明図である。なお、第25
図イは本発明の第1の実施例において得られた
Pb-In系蒸着膜の濃度分布を示す線図、同図ロ
はその格子定数の分布を示す線図、同図ハはその
超電導臨界温度の変化を示す線図であり、第26
図は本発明の第2の実施例において得られたPb-
In-Sn系蒸着膜の濃度分布と超電導臨界温度の
分布を示す線図である。

発明の詳細な説明

本発明は真空蒸着法によつて単元系もしくは複
元系の材料を製造する方法に関し、とくに蒸着基
板上の位置に応じて各成分材料の膜厚もしくは組
成比率が直線的に変化するような材料を1枚の蒸
着膜として得る方法に関するものである。

例えば、冶金学の分野において新しい合金材料
を開発しようとする場合には、各成分材料の組成
比率を広範囲にわたつて変化させ、果してどのよ
うな組成比率の範囲において最良の特性が得られ
るかを試験してみる必要がある。ところで、従来
のように、各成分材料の組成比率が異なる毎に別

別の試料を調製してやるのでは、この試料作成作業にあまりにも多くの時間と労力を費してしまうこととなり、これが新材料の開発を困難にする一因ともなつている。

このため、最近では真空蒸着法によつて一枚の基板上に複数の成分材料を同時に蒸着させるに際して、基板上の位置に応じて各成分材料の蒸着量を変化させることにより、各成分材料の組成比率が蒸着位置に応じて広範囲にわたつて変化するような蒸着膜を得、これを試料として用いる方法が提案されている。

その1は、米国のKENNEDYらの報告 (J. Applied Physics Vol. 36 No. 12, 1965, P. 3808) に見られるものであり、第1図イに示すように、3種類の蒸発源A, B, Cを三角形の蒸着基板Pの頂点a, b, cの直下にそれぞれ配置し、基板P上の位置に応じて各蒸発源からの距離および傾斜角が変化することを利用して、各成分材料の組成比率(以下単に濃度といふ)が場所によつて変化する(つまり濃度分布のある)蒸着膜を得る方法である。しかしながら、この方法によつて得られる各成分材料の濃度分布は、第1図ロにその一例を示すように、通常用いられている3元系状態図のものと比べて分布の直線性が著るしく悪いものとなる。つまり、基板上の位置と各成分材料の濃度とが直線的な比例関係にないので、得られた蒸着膜の位置と材料組成との対応をつけていく欠点がある。

その2は、特公昭43-27926号に見られる方法であり、複数種の帯状蒸発源をほぼ平行または放射状に配列し、該蒸発源のほぼ垂直方向に蒸着基板を配置し、端面にエッジ効果を有する遮蔽板を前記蒸発源と基板との間に相互に半陰影を画くように設け、各蒸発源の半陰影が基板上で互いに反対向きに重なり合うようにして、各蒸発源を同時に蒸発せしめ、もつて基板上に各蒸発源の長手方向に向つて直線的に成分濃度の変化する複元系材料の蒸着膜を得るようにしたものである。

例えは2元系の場合には、第2図イに示すように、直線状蒸発源A, Bを左右一直線上に配列し、これと基板Pとの間にそれぞれ蒸発源A, Bと直角方向(紙面と直角方向)にのびている直線状端面a, bを有する遮蔽板Qa, Qbを設け、端面aによる蒸発源Aの半陰影と端面bによる蒸発源B

の半陰影とが基板上で互いに反対向きに重なり合うようにして、蒸発源A, Bから別々の試料を同時に蒸発せしめて、基板P上に蒸着せしめる。しかるべきは、基板P上には第2図ロに示すような直線状の濃度分布をもつ2元系材料の蒸着膜が得られる。

また、第3図イに示すように、左右両端に蒸発源と直角な端面a', b'をもつ遮蔽板Qを用い、該遮蔽板Qの外周を蒸発物質の通路としたものにおいても、蒸発源A, Bの半陰影を基板P上で互いに重なり合うようにすることによつて第3図ロに示すような直線的な濃度分布をもつ2元系材料の蒸着膜が得られる。

なお、3元系の場合には、第4図イに示すごとく、蒸発面R上の1点uを中心として3種の蒸発源A, B, Cを互いに120°ずつずらせて放射状に配列し、その上方に正三角形の遮蔽板Qを配置し、さらにその上方に正三角形の蒸着基板Pを遮蔽板Qと逆向きに配置して、遮蔽板Qの3辺b'c', c'a', a'b'によつてそれぞれ画かれる蒸着源A, B, Cの半陰影が基板P上で互いに重なり合うようにする。しかるべきは、基板P上には第4図ロに示すような3元状態図型の濃度分布をもつ蒸着膜が得られる。

このように、特公昭43-27926号の方法においては、基板の寸法に比べ蒸発源と基板との距離を十分大きくとつておくことを条件として、各蒸発源の長手方向に向つて直線的な濃度勾配をもつ複元系材料の蒸着膜が得られる。しかしながら、この方法においては、遮蔽板の端面によつて基板上に形成される蒸発源の半陰影を利用して各蒸発源の長手方向に濃度勾配をもたせているため、所望の寸法および濃度分布の蒸着膜を得るために各蒸発源の長さとその両端位置を正確に決めてやる必要があり、蒸発源の製作精度の点で難点がある。

本発明は、このような点に鑑みてなされたもので、上述したような半陰影効果を用いることなく、¹個もしくは複数個の任意長さの直線状蒸発源を用いて、上記各蒸着源と直角な方向に直線的に蒸着膜厚もしくは成分濃度の変化する単元系もしくは複元系材料の蒸着膜を得ることのできる新規かつ独自の方法を提供することを目的とするものである。

すなわち、本発明は1個または複数個の直線状蒸発源と单一の蒸着基板との間に各対応する蒸発源と平行な方向に測つた開口幅が直線的に変化するような1個または複数個の三角形状（もしくはくさび状）の開口部を有するマスクを設け、上記各蒸発源からの蒸発物質を各対応する開口部を通して上記基板上に蒸着せしめることにより、上記基板上に前記の各蒸発源と直角な方向に直線的に蒸着膜厚もしくは成分濃度の変化する単元系もしくは複元系材料の蒸着膜を形成せしめることを特徴とするものである。

つまり、本発明においては、基板上から各対応する三角形状（もしくはくさび状）の開口部を通して各蒸着源を覗きみる際、基板上における視点を上記各蒸着源と直角な方向に移行させるにつれてそこから覗きみることのできる蒸着源の長さが直線的に変化することを利用して、その方向に向つて各蒸発源からの材料の蒸着量（膜厚もしくは濃度）が直線的に変化する蒸着膜を得ることを基本原理とするものである。

以下、本発明の実施の態様につき図面を参照して詳説する。

まず最初に、本発明の方法にしたがつて直線的な膜厚変化を有する1元系材料の蒸着膜を得る場合について説明する。

第5図イは、本発明にしたがつて直線的な膜厚変化を有する1元系材料の蒸着膜を得る場合の蒸着装置の原理的配置構成を示すもので、同図中Aは蒸発源、Qはマスク、Pは蒸着基板を示している。基板PとマスクQとは蒸発源Aを含む平面（以下蒸発面といふ）Rと平行に、それぞれそれから h_1 、 h_2 なる間隔をおいて配置され、これらは同一の真空容器（図示せず）内に収容されている。蒸発源Aは直線 ℓ_1 と直角方向にのばされた幅のせまい直線状のものであり、その蒸着量はどこでも均一なものとする。而してマスクQには頂点 a' と蒸発源Aに平行な底辺 $b'c'$ （長さ ℓ_2 ）を有する三角形の開口部Maが設けられている。したがつて、蒸発源Aと平行な方向に測つた開口幅は蒸発源Aと直角な方向（直線mの方向）に0から ℓ_2 まで直線的に変化する。なお、蒸発源Aと直角な方向に測つた開口部Maの長さは b_2 であるとする。

また、基板Pの蒸発源Aと直角方向（直線nの方向）の長さは d_1 、平行方向の幅は ℓ_1 であり、

$d_2/d_1 = h_2/h_1$ なる関係が成立するものとする。そして、蒸着源Aと開口部Maの底辺 $b'c'$ と基板Pの右端 p_1 とは互いに同一平面上にあり、また、蒸着源Aと開口部Maの頂点 a と基板Pの左端 p_3 とは互いに同一平面上にあるようとする。なお、基板Pと蒸発源Aとの距離 h_1 は基板Pの寸法 d_1 、 ℓ_1 に對して十分大きく（数倍以上に）とつてある。

この状態で蒸発源Aから所望の材料を蒸発させると、基板P上には、第5図ロに示すように、蒸発源Aと直角な方向に直線的に膜厚が変化し、蒸発源Aと平行な方向には膜厚変化のない蒸着膜が得られる。すなわち、いま基板P上に蒸発源Aと直角な方向に p_1 、 p_2 、 p_3 なる3視点を考えた場合、 p_1 点から蒸発源Aを覗うときの実効的な開口幅は ℓ_2 であり、中間点 p_2 からのそれは $\ell_2/2$ 、 p_3 点からのそれは0である。したがつて、 p_1 点からは蒸発源Aのうち $L = \frac{h_1}{h_1 - h_2} \times \ell_2$ なる長さの部分が覗かれ、 p_2 点からは $L/2$ なる長さの部が覗かれ、 p_3 点からは蒸発源Aのいかなる部分も覗けなくなる。而して、基板P上の任意の点の膜厚はその点から開口部Maを通して覗くことのできる蒸発源Aの長さに比例するから、 p_1 点での膜厚を100とすると p_2 点での膜厚は50、 p_3 点でのそれは0となる。このように、蒸着膜厚は蒸発源Aに直角な方向に向つて直線的に変化する。

つぎに、基板P上に p_1 点を通つて蒸発源Aに平行な直線を考えた場合、この直線上のいずれの点から蒸発源Aを覗うとしても実効的な開口幅は常に ℓ_2 である。したがつて、この線上から覗くことのできる蒸着源の長さは常に L であり、その中心位置だけが基板上の視点位置に對応して蒸発源の長手方向に移行する。また、 p_2 点を通つて蒸発源Aに平行な直線を考えた場合、この直線上のいずれの点に視点を移しても実効的な開口幅は常に $\ell_2/2$ であり、この線上から覗くことのできる蒸着源の長さは常に $L/2$ である。同様に、 p_3 点を通り蒸発源Aに平行な直線上では、どの点からも全く蒸発源を覗くことができない。したがつて、蒸着膜厚は蒸発源Aと平行な方向には全く変化しない。

以上の説明からわかるように、本発明によれば1個の直線状蒸発源と1個の三角形状の開口部を

有するマスクとを用いて基板上において蒸発源と直角な方向に直線的な膜厚変化を有し、蒸発源と平行な方向には膜厚変化のない蒸着膜を得ることができ。而して、本発明の方法においては、従来方法におけるように半陰影部分を用いて蒸着膜の膜厚変化をつけることをしないので、蒸発源の長さに任意性があり、したがつてその製作上の自由度が大である。すなわち、蒸発源の長さは、前述した p_1 点において覗くことのできる長さ $L = \frac{h_1}{h_1 - h_2} \times \ell_2$ に基板 P の幅 ℓ_1 に対応する視野中心のずれ $dL = \frac{h_2}{h_1 - h_2} \times \ell_1$ を加えた値 $\ell_3 = \frac{h_1 \ell_2 + h_2 \ell_1}{h_1 - h_2}$ よりも大でありさえすればいかなる長さでもよい。

なお、基板上の位置によつて蒸発源までの距離および傾斜角が相異することによつて生じる膜厚分布の直線性からのずれを無視し得る程度に小さくするためには、基板の寸法 d_1, ℓ_1 に対して基板距離 h_1 を数倍以上に選ぶのがよい。

一例として、第5図イの配置構成において、

$h_1 = 30\text{ cm}$, $h_2 = 10\text{ cm}$, $d_1 = 9\text{ cm}$, $\ell_1 = 2\text{ cm}$ 20
 $\ell_2 = 2\text{ cm}$ とすれば、 $d_2 = 3\text{ cm}$, $L = 3\text{ cm}$, $\ell_3 = 4\text{ cm}$ となる。このような設定のもとで、蒸発源 A として、長さ 5 cm 幅 3 mm のポート形ヒータを用いて実際にインジウムを基板 P 上に蒸着させたところ所望どおり第5図ロに示すような直線的25
膜厚分布を呈するインジウム薄膜が得られた。一般に、高真空の排気系を用い、基板の加熱または冷却などを行つて蒸発物質の基板への付着率を高め、表面移動を少くしてやれば、再現性のよい膜厚分布が得られる。

なお、上記の説明においては、マスクの開口部 Ma として三角形状のものを用いる例について示したが、この開口部はまた第6図に示すように底辺 $b'c'$ を有しないくさび状のものであつてもよい。要は、このくさび状開口の中に頂点 a' から蒸発源 A に直角な方向に測つて $d_2 = h_2/h_1 \times d_1$ なる範囲にわたつて蒸発源 A と平行な方向に測つた開口幅が直線的に変化する部分 Ma を有していればよい。すなわち、所定寸法の基板 P 上から外れた位置から蒸発源 A のどれだけの長さが覗かれよう40
とそれは基板 P 上の膜厚分布には無関係であるからである。したがつて、 d_2 なる長さが確保され45
てさえいれば、それを越える開口部分は有つてもなくともよいものである。このことからまた、 d_2

を越える開口部分が有つたとしても、その部分はいかなる形状であつてもよいといふことがわかる。第7図イは所要寸法の開口部 Ma をそのままの頂角で右方に延長した例を示し、第7図ロは菱形の開口の半分をもつて所要寸法の開口部 Ma とした例を示し、第7図ハは所要寸法の開口部 Ma の右端を矩形状に延長した例を示す。

また、開口部 Ma は必ずしも頂点 a をとおり蒸発源 A と直角に引かれた直線 m に沿つてのびるものである必要はなく、第8図イ、ロに示すように、直線 m と傾斜する方向にのびているものでもよい。ただし、この場合には、基板 P も同じ方向に傾斜させるか、あるいは蒸発源の長さを十分大きくとする必要がある。

さらに極端な場合には、開口部 Ma は第9図イに示すように途中で不連続に折れ曲つているものでもよく、第9図ロに示すように曲線状に彎曲したものでもよい。要は d_2 なる長さにわたつて開口幅が直線的に変化するものであれば足りる。

このように、蒸発源 A の長さを十分大きくとれば、開口部の形状はかなり任意に選定できる。以下の説明においては主として三角形の開口部を用いる場合について説明するが、本発明は上述したような変形をも含むものであることはいうまでもない。

また、上記の説明においては基板 P として長方形のものを用いる例を示したが、この基板 P の形状もそれ自体単独にもしくは開口部の形状に応じてかなり任意に選定できる。第10図は三角形の30
基板を用いた例を示し、第11図は同じく三角形の基板を用いたものにおいて開口部 Ma の中心線を m から m' へ傾けたのに伴つて基板 P の方向も n から n' へ傾けた例を示す。

さらに、上記説明においては、1個の蒸発源と1個の開口部を用いる例について示したが、同一材料を蒸発させる複数個の蒸発源とこれに対応する複数個の開口部とを用いてもよい。第12図および第13図はいずれも2個の蒸発源 A, A' と2個の開口部 Ma, Ma' を有するマスクとを用いて单一の基板 P 上に蒸着させる例を示すもので、前者は蒸発源 A, A' を平行に配置した一例、後者は一直線上に配置した一例である。

つぎに、上述の原理を応用して成分濃度が直線的に変化する2元系材料の蒸着膜を得る方法につ

いてのべる。

第14図イは、本発明の方法にしたがつて、2元系材料の蒸着膜を得る場合の蒸着装置の原理的配置構成を示すもので、同図中A, Bは互いに異種の材料を蒸発せしめる蒸発源、Ma, Mbはそれぞれ蒸発源A, Bに対応する開口部、Pは蒸発基板を示している。而して、開口部MaとMbとは直線mを中心にして互いに逆向き(背中合せ)に配置されている。ここで、蒸発源A, B間の距離を r_1 ・開口部Ma, Mb間の間隔を r_2 とし、前述した $d_1/d_2 = h_2/h_1$ なる条件の外に、 $(h_1 - h_2)/h_1 = (d_2 + r_2)/r_1$ なる関係をも満すように各部の寸法を設定する。一例として、 $h_1 = 30\text{ cm}$, $h_2 = 10\text{ cm}$, $d_1 = 9\text{ cm}$, $\ell_1 = 2\text{ cm}$, $\ell_2 = 2\text{ cm}$, $r_1 = 9\text{ cm}$ とすれば、 $d_2 = 3\text{ cm}$, $\ell_3 = 4\text{ cm}$, $r_2 = 3\text{ cm}$ となる。

このような条件のもとで、蒸発源A, Bから2種の材料を同時に蒸発させると、基板P上には2種の材料が重なり合つて蒸着され、第14図ロに示すような濃度分布の蒸着膜が得られる。すなわち、蒸発源Aからの材料(A成分)の蒸着量は p_2 点から p_1 点に向つて0から100まで直線的に変化する。また、蒸発源Bからの材料(B成分)の蒸着量は反対に p_1 点から p_2 点に向つて0から100まで直線的に変化する。そして、上記両成分の全蒸着量を重量で等しくとるとときは、得られる濃度分布は重量パーセントで直線状に変化するものとなり、また両成分の全蒸着量を原子数もしくは分子数で等しくとるとときは得られる濃度分布は原子パーセントもしくは分子パーセントで直線的に変化するものとなる。これはまた、蒸発源A, Bの蒸発速度を制御することによつても任意に調節できる。

このように、本発明の方法によれば、2種の蒸発源と互いに逆向きの2個の開口部を有するマスクとを組み合せることによつて、単一の基板P上に両蒸発源と直角方向に向つて直線的に濃度分布の変化する2元系材料の蒸着膜を得ることができる。

なお、第15図イに示すように、開口部Ma, Mbを互いにその頂点を向い合せるようにして逆向きに配置した場合にも、やはり第15図ロに示すように両蒸発源と直角な方向に直線的な濃度分布を有する2元系材料の蒸着膜が得られる。

また、第16図に示すように、蒸発源を近づけることにより $r_2 = 0$ にして開口部MaとMbを連結させちようど1個の菱形状の開口となるようにしてもよいし、第17図に示すように、 h_1 と h_2 の比を変えることによつて開口部MaとMbの頂点が一致するようにしてもよい。なお、第17図において、開口部MaはMa'に等価であり、開口部MbはMb'に等価であることがわかる。このことからまた、開口部はMaとMb, MaとMb', Ma'とMb, Ma' and Mb'のごとき任意の組合せとしてもよいことがわかる。

さらにまた、第18図に示すように、蒸発源A, Bを一直線上に配置し、開口部Ma, Mbを互いに逆向きにして蒸発源と平行方向に並べ設けてもよし、さらには、第19図に示すように、開口部MaとMbを背中合せに配置したものにおいて、両者をその所要長さ d_2 を越えて内方に延長し、全体として菱形をした单一開口を用いてもよい。

つぎに、本発明の方法にしたがつて成分濃度が直線的に変化する3元系材料の蒸着膜を得る場合についてのべる。

第20図イは、本発明の方法にしたがつて3種の蒸発源A, B, Cと単一の開口Moを有するマスクQとの組合せを用いて、単一の基板P上に3元系材料の蒸着膜を形成させる例を示している。ここで、蒸発源A, B, Cは三角形 $\alpha\beta\gamma$ の各辺をなすように配置されている。開口Moは上記の三角形 $\alpha\beta\gamma$ と相似する三角形 $a'b'c'$ の形をしている。また、基板Pは上記三角形 $a'b'c'$ と相似する三角形 abc を呈している。而して、三角形 abc と三角形 $a'b'c'$ との相似比は、 h_1/h_2 であり、三角形 $\alpha\beta\gamma$ と三角形 $a'b'c'$ との相似比は $h_1/(h_1 - h_2)$ である。一例として、一辺の長さが10cmの正三角形基板を用い、 $h_1 = 30\text{ cm}$, $h_2 = 15\text{ cm}$ とすると、開口Moは一辺の長さが5cmの正三角形状のものとなり、各蒸発源の所要長さは10cmとなる。

このような条件のもとで、蒸発源A, B, Cから3種の材料を同時に蒸発させると、基板P上には、第20図ロに示すような濃度分布の3元系材料が蒸着される。すなわち、蒸発源Aに対しては三角形開口Moは a' を頂点とし $b'c'$ を底辺とする開口部Maとして働く、基板P上のA成分の濃度を a 方向に直線的に変化せしめる。同様に蒸

発源B, Cに対しては開口Moはそれぞれb', c'を頂点とする開口部M_b, M_cとして働き、基板P上のB, C成分の濃度をそれぞれb_e, o_f方向に直線的に変化せしめる。

なお、蒸着は必ずしも3種の材料を同時に蒸発させて行なう必要はなく、順次にもしくは交番的に蒸発させるようにしてもよいことはいうまでもない。また、基板Pの形状も正三角形に限るものではないことは1元系材料についての説明から容易に理解されるところである。このことは、ある特定の成分材料について濃度勾配をゆるやかにしてわずかな濃度変化による材料特性の差を調べる場合に有利である。

なお上記の説明においては、5種の蒸発源A, B, Cを三角形 $\alpha\beta\gamma$ の各辺の長さと等しく選んでいるため、各頂点位置で2種の蒸発源が互いに端部を接することになり、蒸発源が作りにくくなるきらいがある。これを避けるためには第21図に示すようにすればよい。すなわち、第21図は、本来三角形 $\alpha\beta\gamma$ 上に互いに端部を接して配置されていた蒸発源A, B, Cをそのままの長さでK倍($K \geq 1$)の三角形 $\alpha'\beta'\gamma'$ の各辺の中央部に移動させ、これに伴つて本来Moであつた開口をMo'のごとく($K+1$)/2倍に拡大した場合を示している。つまり、蒸発源A, B, Cを三角形 $\alpha'\beta'\gamma'$ 上にずらせたことにより、各蒸発源に対応する開口部の所要寸法は元の開口Moの寸法と変わらないが、その各頂点はそれぞれa', b', c'にずれて、全体としては拡大された開口Mo'となつてゐたとえば、蒸発源Aに対しては開口Mo'のうち三角形a''b''c'''なる部分(これはMoと同一寸法)が所要の開口部Maとなる。このようにすれば、3種の蒸発源はその所要長さLの範囲内では互いに接触しなくなる。したがつて、各蒸発源の所要長さを十分確保することができ、製作が容易となる。

なお、上記の例においてK=3とすれば、開口Mo'の寸法はK=1のときの開口Moの所要寸法の2倍となる。したがつて、K>3とすれば、第22図に示すように、各蒸発源A, B, Cに対してそれぞれ別々の開口部Ma, Mb, Mcをもつたマスクを用いることができる。

さらにまた、第23図に示すように、本来三角形 $\alpha\beta\gamma$ 上に配置されていた蒸発源A, B, Cをそのままの長さで逆向きの三角形 $\alpha''\beta''\gamma''$ 上に移

動させ、これに伴つて本来1個であつた開口Moの代りに各蒸発源A, B, Cにそれぞれ対応する3個の開口Ma, Mb, Mcを設けてよい。なお、この場合にも、3個の蒸着源が互いに接触しないようにするために各蒸発源を三角形 $\alpha'\beta'\gamma'$ の各辺よりいくぶん外方はずらせてやるのがよく、そのときはマスクの開口Ma, Mb, Mcも対応して外方はずらせてやればよい。

以上の考察から次のようなことがわかる。すなわち、第24図に示すように、3種の蒸発源A₁, B₁, C₁と単一の開口M₁との組合せにより単一の基板P上に3種の材料を蒸着せしめる場合(つまり第20図の場合)において、開口をM₄へ移動せば、蒸発源はA₄, B₄, C₄へ移動し、M₅へ移動せばA₅, B₅, C₅へと移動する。したがつて、A₁, B₁をそのままにしてC₁のみをC₄へ移してA₁, B₁, C₄なる蒸発源の組合せとすれば、開口A₁, B₁に対応するM₁とC₄に対応するM₄との2個の組合せとなる。この状態からさらに、A₁をA₅へ移してA₅, B₄, C₄なる蒸発源の組合せとすれば、開口の組合せはM₅, M₁, M₄の3個となる。そして、この組合せは第21図においてK=3ととつた場合に当る。同様に、蒸発源をA₄, B₆, C₅の組合せとするとときは、開口の組合せはM₄, M₆, M₅となり、これは第23図に示した場合に当る。

而して、今度は逆に開口の組合せをM₁, M₂のごとく先に設定すれば、蒸発源としてはA₁, A₂, B₁, B₂, C₁, C₂の6個の組合せを用いてよいし、これらのうちから各材料につき任意の1個づつをとる3個の組合せとしてもよい。同様に、開口の組合せをM₁, M₂, M₄の3個とするときは、蒸発源としてはA₁, A₂, A₄, B₁, B₂, B₄, C₁, C₂, C₄のごとき9個の組合せとしてもよいし、これらのうちから各材料につき任意の2個づつをとる6個または任意の1個づつをとる3個の組合せとしてもよい。このように、開口の個数を増していくことにより、蒸発源の組合せ方は無数に増えていく。

なお、上記は3種の材料につき互いに同数の蒸発源を組合せる場合について示したが、各材料の蒸着量に差をもたせるときは、各材料についての蒸発源の数に差をもたせることができる。例えば、第24図において、開口部としてはM₁とM₂の2個を用い、蒸発源としてはA, B成分に

ついては A_1, A_2, B_1, B_2 のごとく各 2 個づつを、C 成分については C_1, C_2 のどちらか一方を用い、この C 成分についての蒸発源の蒸発量を A, B 成分のそれの 2 倍にしておけばよい。

以上、本発明の方法により 1 元系、2 元系および 3 元系の材料を製造する場合について説明してきたが、本発明の方法はさらに 4 元系以上の多元系材料を得る場合にも適用できるものであることは容易に理解されよう。例えば、4 元系の場合には 3 元系の蒸着膜の上に第 4 の材料を重ねて蒸着してもよく、あるいは 4 種の蒸発源と 4 個のくさび状開口部（もしくは四角形の開口部の各頂点位でもよい）との組合せを用いて同時に蒸着してもよい。なお、拡散処理の可能な系においては、蒸着後の熱処理により膜厚方向の組成の均一化を計ることもできる。

而して、本発明における直線状蒸発源としては、例えば所望の材料の線材そのものを直接加熱蒸発させるものでもよく、線状もしくはエイル状のヒータの表面に所望の材料を塗布、メッキなどの方法により被覆したものを用いてもよく、あるいは線状ヒータと所望の材料を撚り合せたものを用いてもよいし、幅のせまいポート型ヒータを用いてもよい。また、蒸着基板としてはガラスその他セラミック、金属板、シリコンや塩化ナトリウムのへき開面などを用いることができ、マスクとしてはモリブデンなどの金属板のほかガラスやセラミックなどを用いてもよい。

以下に本発明の実施例についてのべる。

実施例 1

まず、 $Pb-In$ 2 元合金系の状態図型濃度分布を有する試料を得る場合についてのべる。

第 15 図イに示す配置構成において、 $h_1 = 30$ cm, $h_2 = 10$ cm, $d_1 = 9$ cm, $d_2 = 3$ cm, $\ell_1 = 2$ cm, $\ell_2 = 2$ cm, $r_1 = 9$ cm, $r_2 = 3$ cm とし、蒸発源 A, B としては長さ 5 cm、幅 3 mm の帯状のポート型ヒータを用い、基板 P にはスライドガラスを用い、マスク Q にはモリブデン板を用いた。ポート A, B にはそれぞれ純度 99.999% の鉛塊、インジウム塊を重量で原子量比 (207 : 115) となるように秤量して挿入し、ベルジャーネ内を 10^{-6} mmHg 程度の真空中に排気した。この状態でまずポンバードを行つて基板表面を清浄にしてから、ポート A, B のヒーター抵抗に直

流または交流を徐々に流して予備加熱を行ない、ポート内の鉛塊またはインジウム塊が溶けてポート上に均一に拡がつてから、予めマスクの開口部 Ma, Mb を塞いでいたシャッターを開くと共に、ヒータ電流をほぼ一定に保つて、蒸着を行つた。ついで、ポート上の材料がほぼ完全に消失するのを見計つて、ヒータ電流を断ち、基板温度が室温に戻るのを待つてから、真空を破つて基板 P を取り出し、さらにこれを電気炉に入れて 1×10^{-6} mmHg 程度の真空中で $150^{\circ}\text{C} \times 2$ 時間の拡散熱処理を行つた。

かくして得られた蒸着膜を基板ごと長手方向に適当な間隔で切り離し、各小片について Sloan 社製のオングストローメータで膜厚分布を、X 線マイクロアナライザーで合金組成比（原子%）を、デバイシエラー X 線分析法で結晶構造の固定を、さらに四端子抵抗法により超電導臨界温度 T_c をそれぞれ測定した。その結果、蒸着膜の濃度分布は第 25 図イに示すように非常に良好な直線性を示した。また、結晶の格子定数や軸比の変化は第 25 図ロに示したとおりであり、臨界温度 T_c の変化は第 25 図ハに示すとおりであつた。このように、得られた蒸着膜中の各成分の濃度分布は基板の長手方向（つまり蒸発源と直角な方向）の位置と直線的な比例関係にある。

実施例 2

つぎに、 $Pb-In-Sn$ の 3 元状態図型濃度分布の試料を得る場合についてのべる。

第 21 図イに示す配置構成において、 $b_1 = 30$ cm, $h_2 = 15$ cm とし、基板 P としては一辺の長さが 10 cm の正三角形のガラス板を用い、またマスクとしては一辺の長さが 5.5 cm の正三角形開口 Mo' を有するモリブデン板を用いた。また、蒸発源 A, B, C としては、それぞれ長さ 11 cm, 幅 3 mm のポート型ヒータを用い、これを一辺の長さが 12 cm の正三角形 $\alpha\beta\gamma$ の各辺の中央部に配置した。ポート A, B, C にはそれぞれ純度 99.999% の In, Pb, Sn を重量比がそれらの原子量比 (115 : 207 : 119) と等しくなるように秤量して挿入し、以下は前記実施例と同様にして蒸着および熱処理を行なつた。

その結果得られた蒸着膜の濃度分布は第 26 図に示すように通常の三元状態図のものと非常に良く一致している。なお、第 26 図中の数字は各組

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成比における超電導臨界温度を測定した結果を示している。

以上詳説したところから明らかかなように、本発明の方法によれば、1個または複数個の直線状蒸発源とこれらの蒸発源の長手方向に平行な開口幅5が直線的に変化する1個または複数個の開口を有するマスクとを用いることによつて、基板上に各蒸発源と直角な方向に直線的な蒸着量変化を有する単元系もしくは複元系の材料を得ることができるものであり、従来の半陰影を用いる方法とは原理的に異なるものである。したがつて、蒸発源としてはある所要の長さ以上あればいかなる長さのものでもよいので蒸発源の製作が容易であり、また基板の形状や蒸発源の配置の自由度も大となる等の長所を有するものである。

16

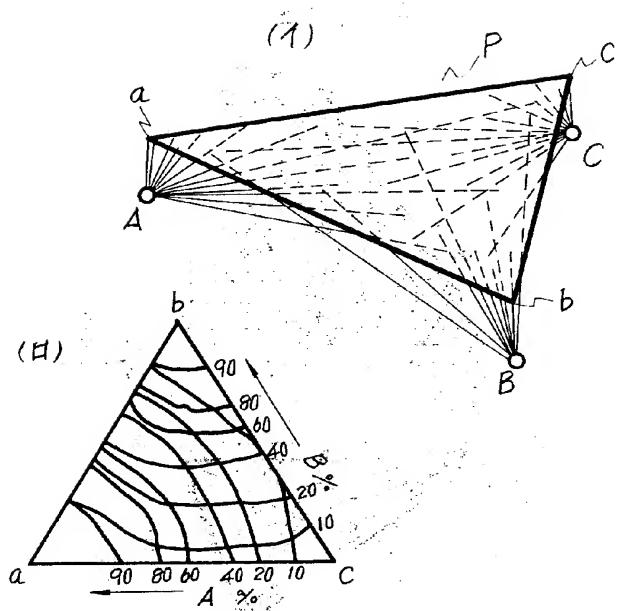
なお、本発明の方法は、単に合金試料の作成にのみ用いられるものではなく、通常蒸着の可能なすべての材料の任意の組合せについて適用できるものであることはいうまでもない。

⑤特許請求の範囲

1 1個または複数個の直線状蒸発源と单一の蒸着基板との間に各対応する蒸発源と平行な方向に測つた開口幅が直線的に変化するような1個または複数個の三角形状もしくはくさび状の開口部を有するマスクを設け、前記の各蒸発源からの蒸発物質を上記の各対応する開口部を通して前記の基板上に蒸着せしめることにより、前記の基板上に前記の各蒸発源と直角な方向に直線的に蒸着膜厚もしくは成分濃度の変化する蒸着膜を得ることを

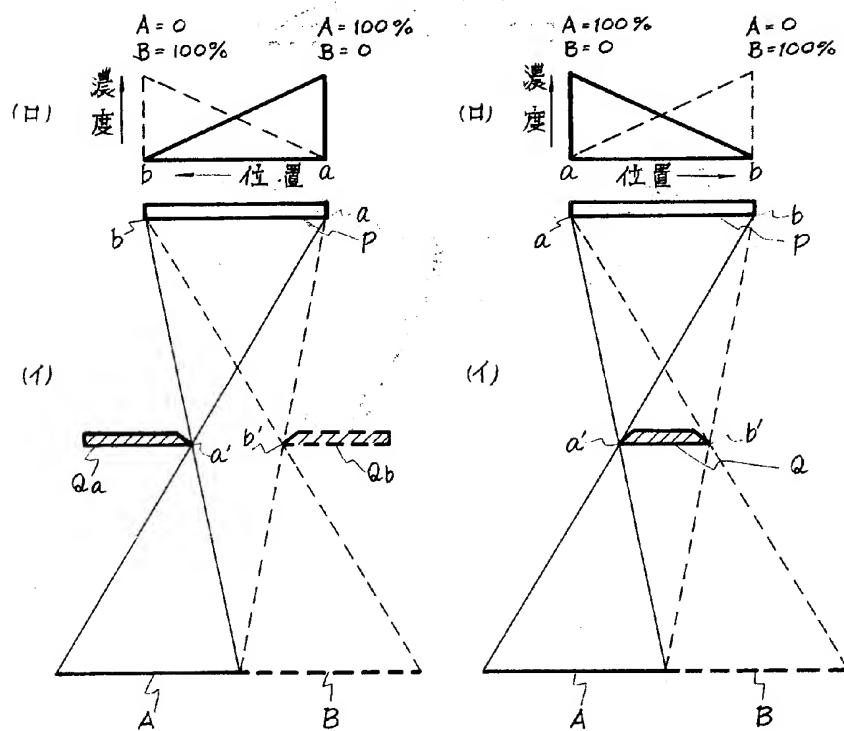
15 特徴とする単元系もしくは複元系材料の製造方法。

＊1図

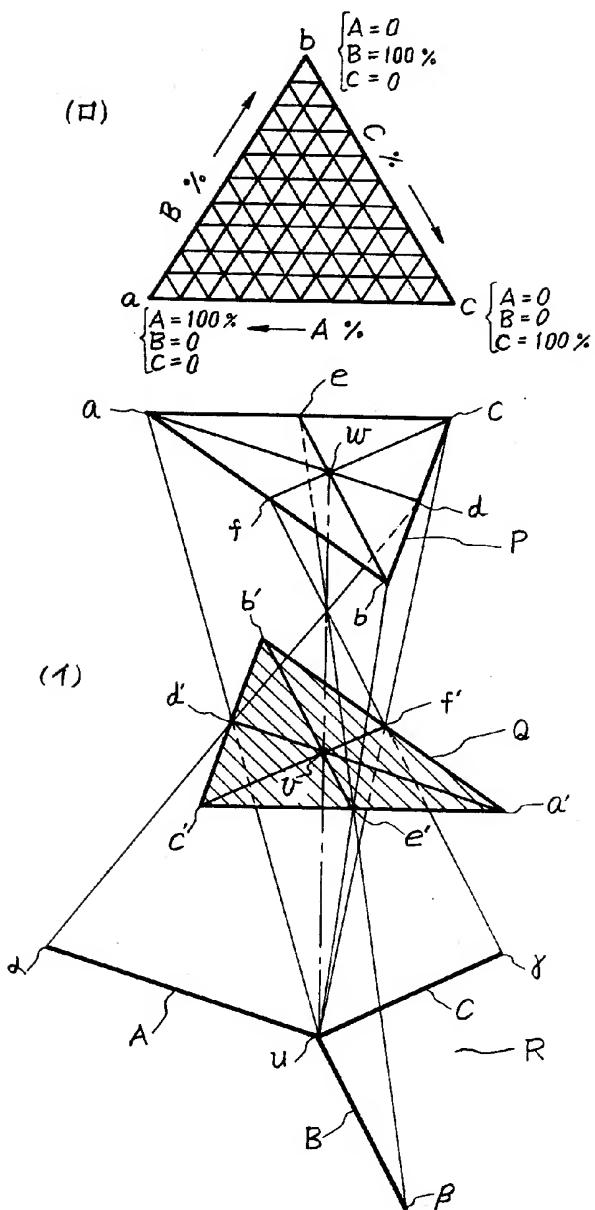


＊2図

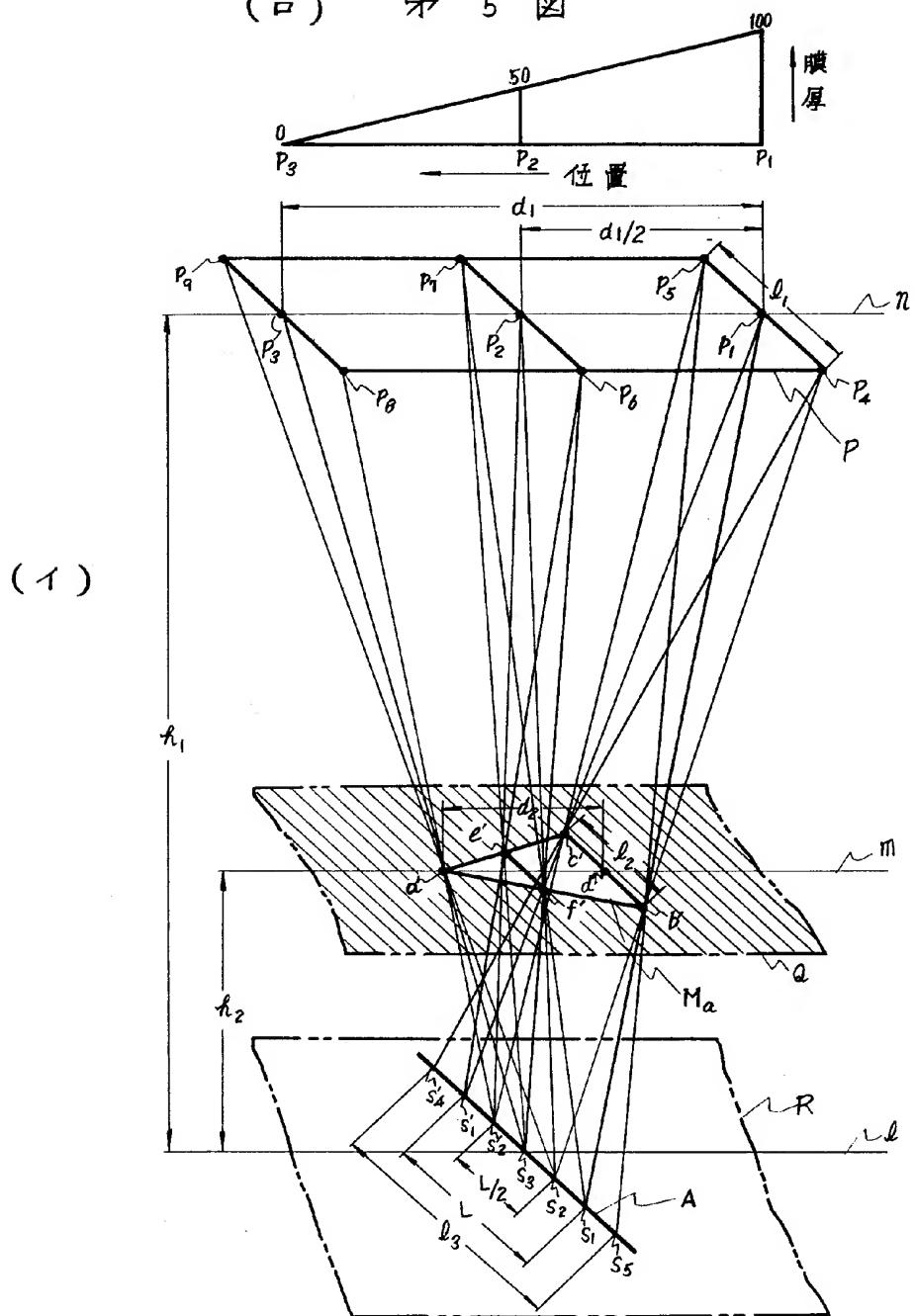
＊3図



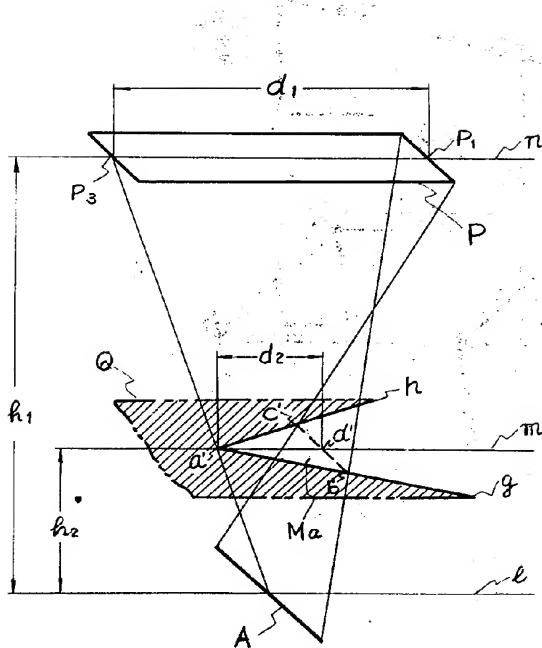
米 4 圖



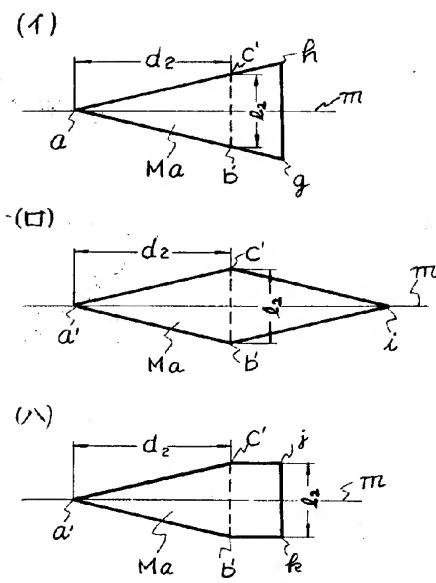
(口) 5 図



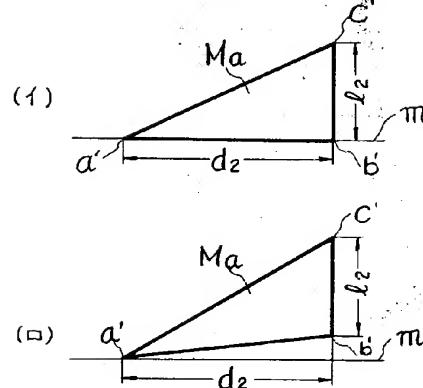
* 6 図



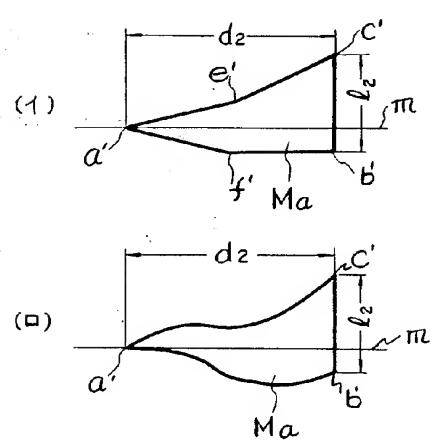
* 7 図



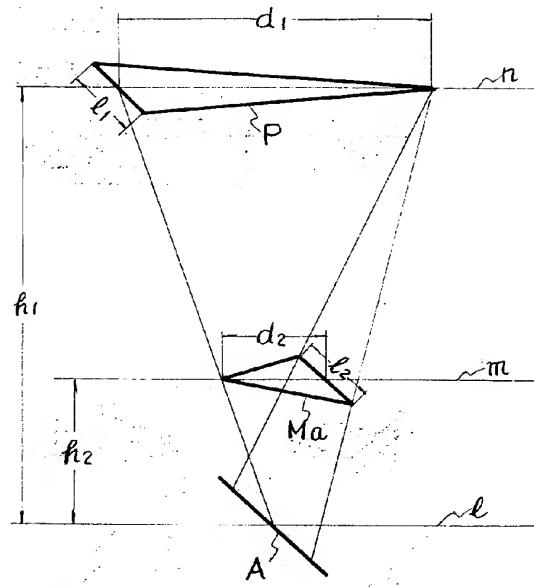
* 8 図



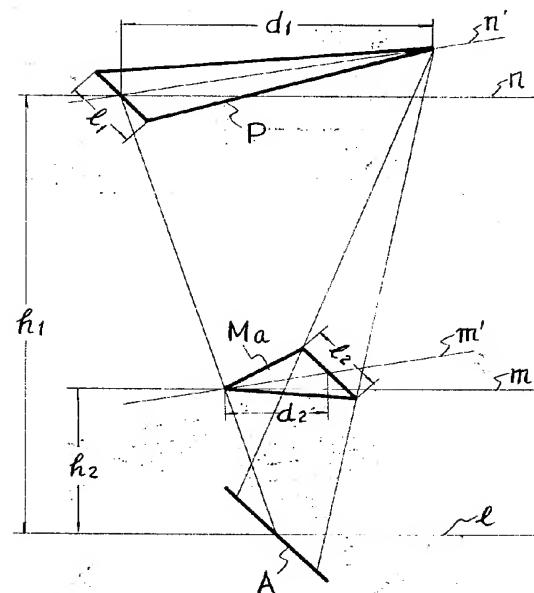
* 9 図



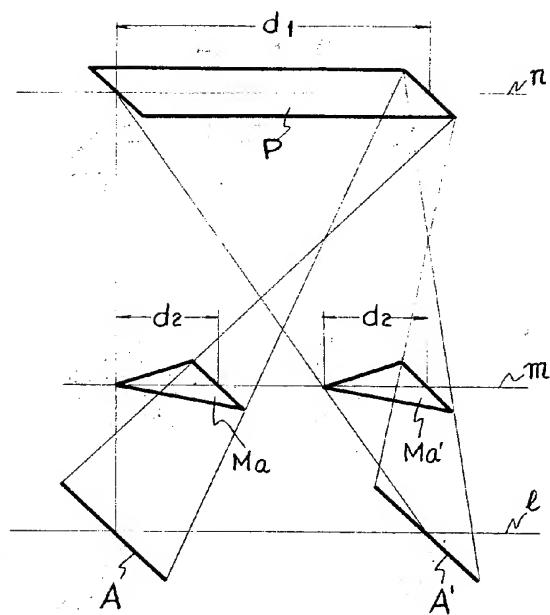
#10図



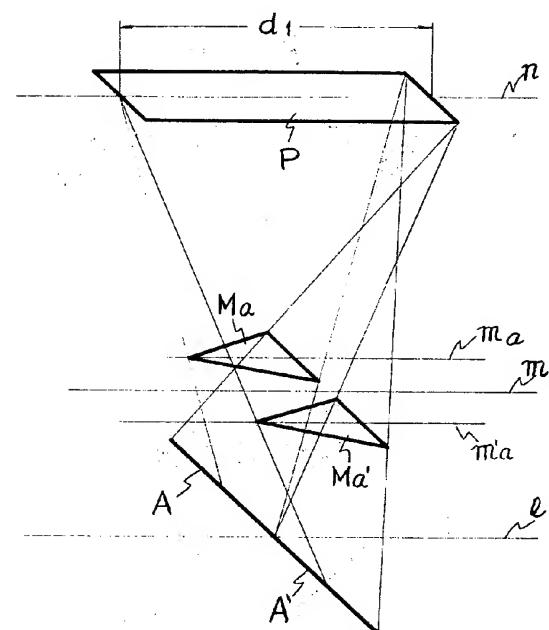
#11図



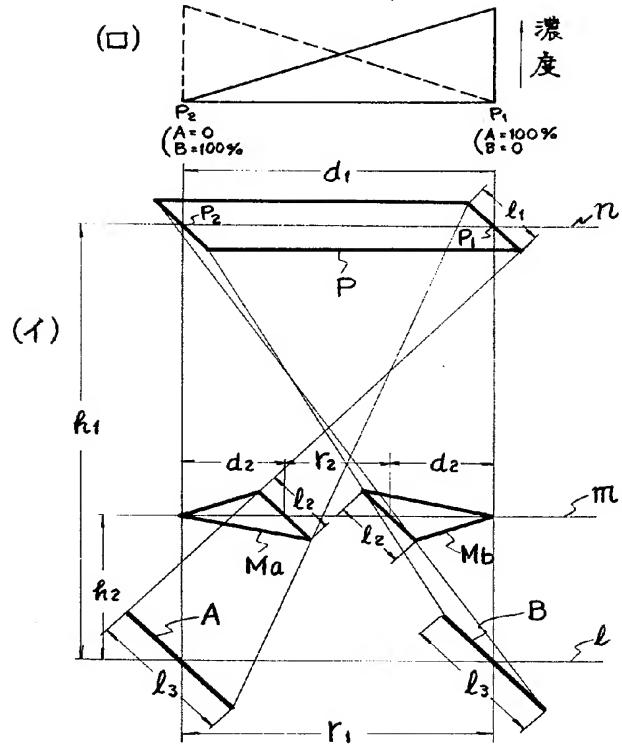
#12図



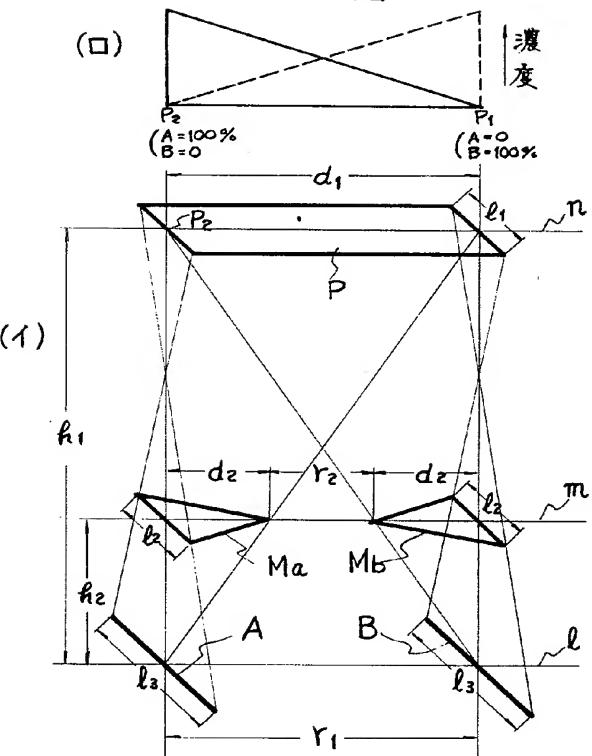
#13図



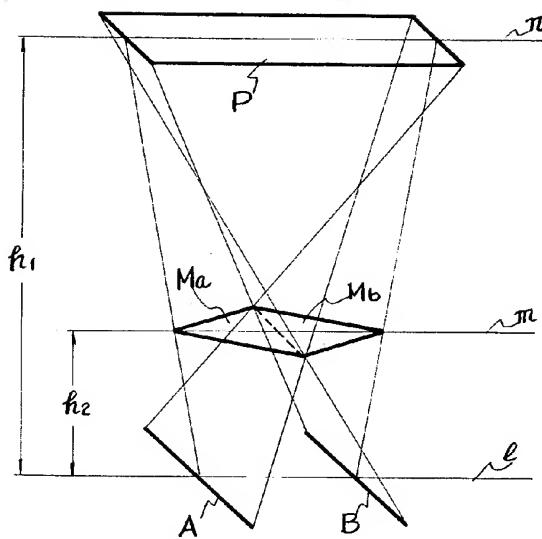
米 14 図



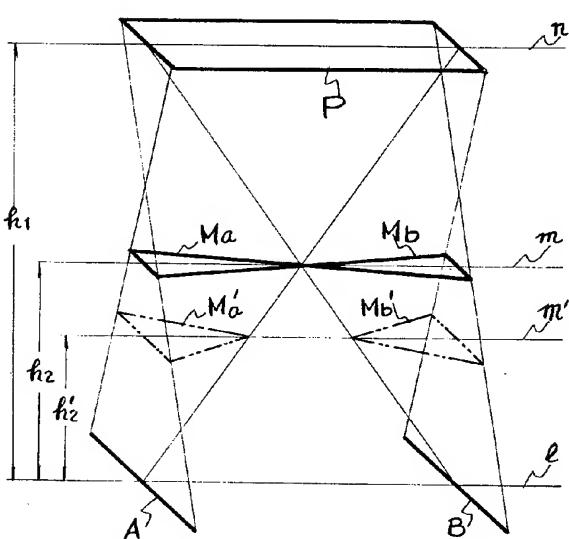
第15回



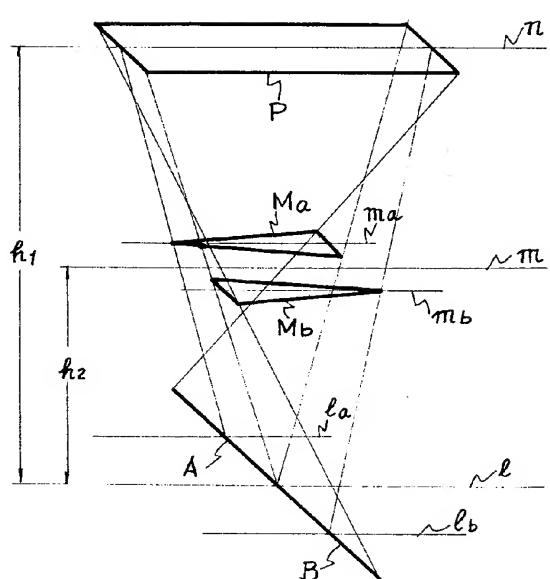
*16 図



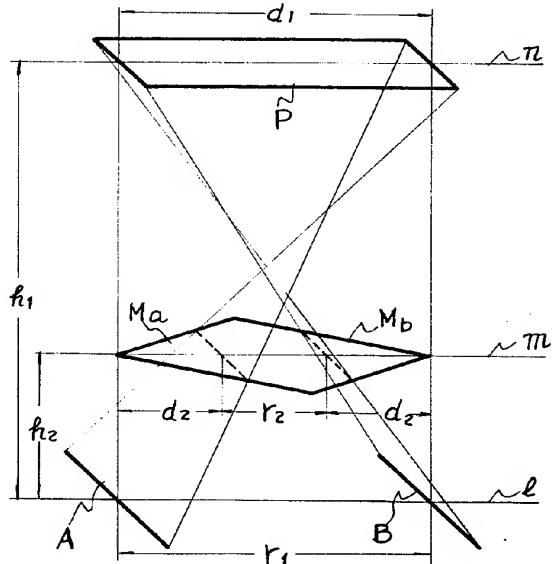
半17回



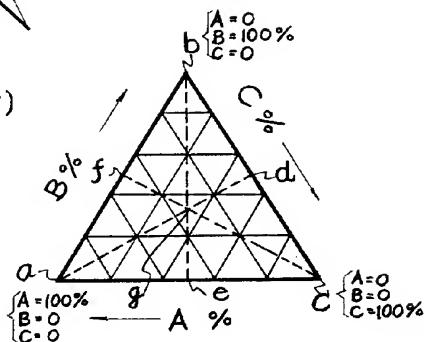
米 18 図



* 19 図

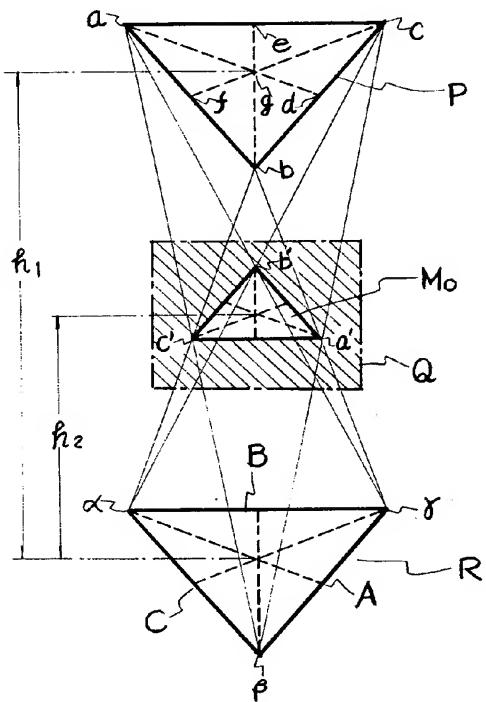


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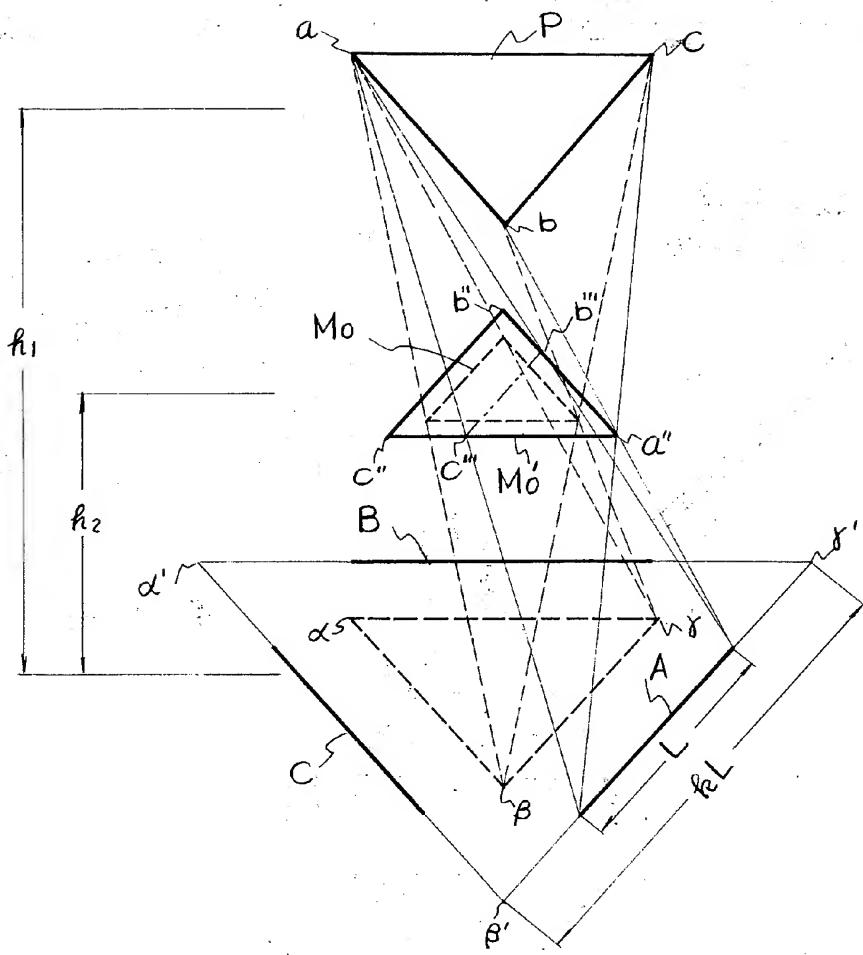


米20 図

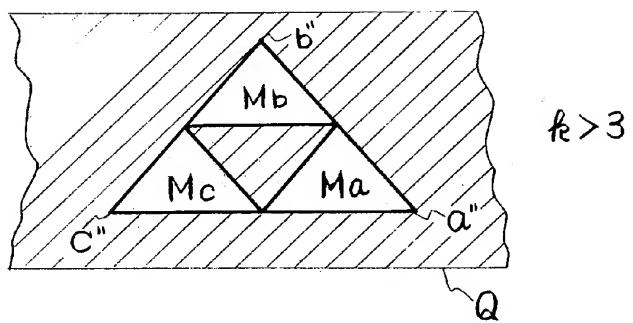
(1)



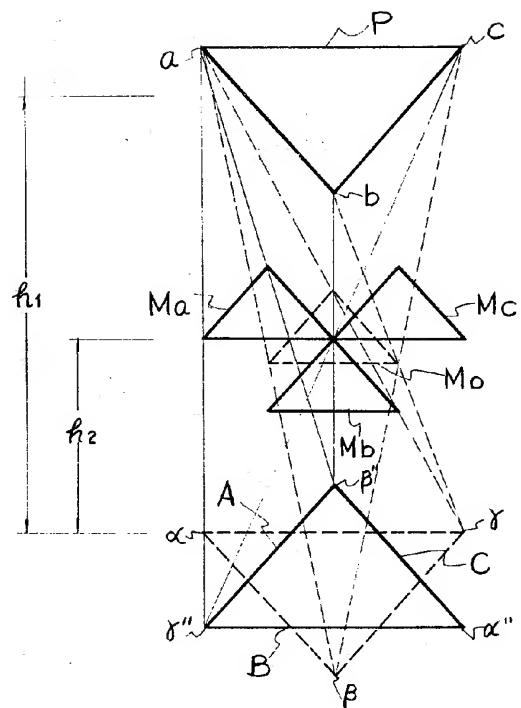
21 図



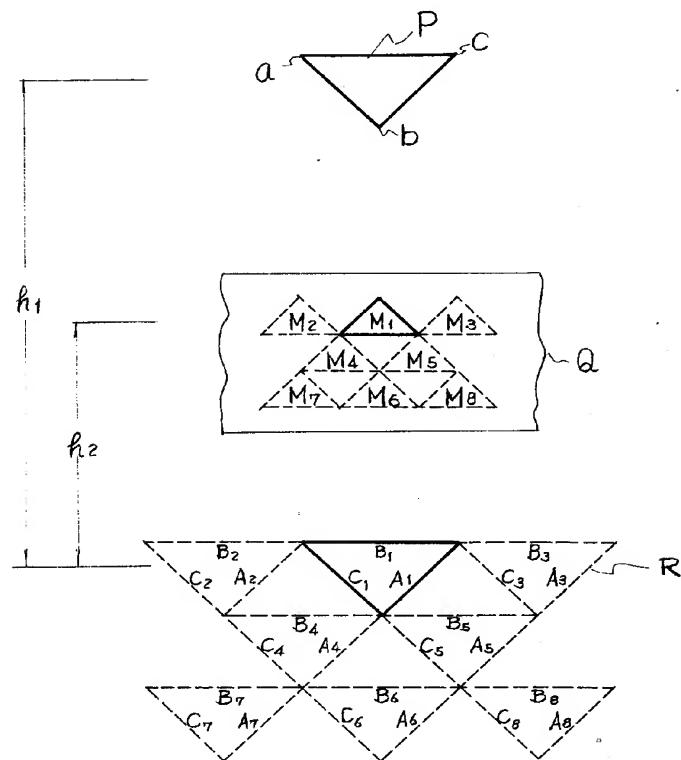
22 図



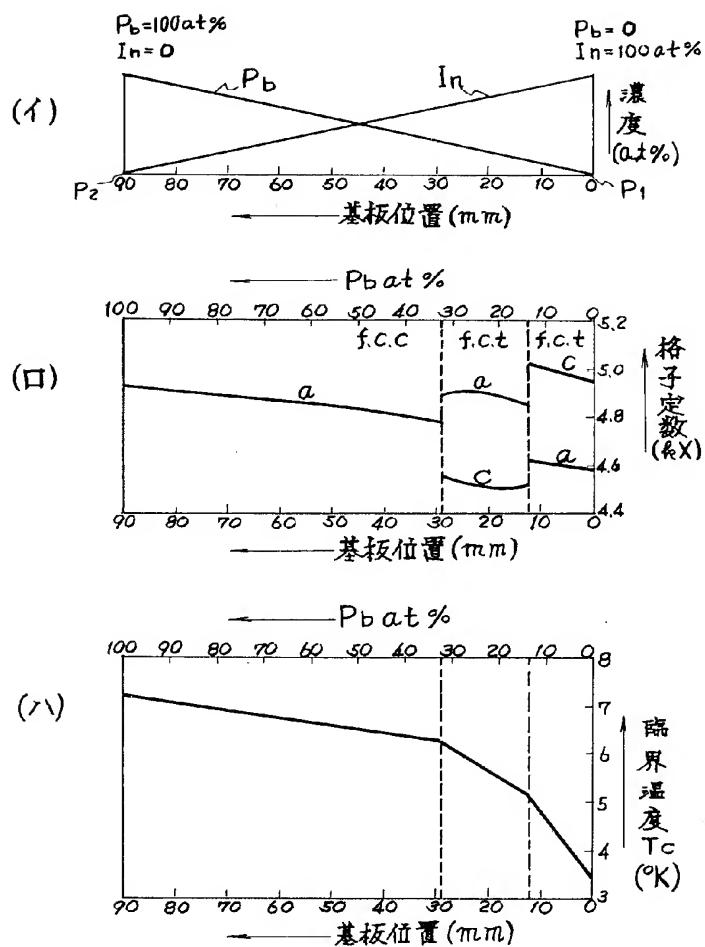
* 23 図



* 24 図



第25図



第26図

